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STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

April 15, 1967

Technical Progress Report 67-1 Semiannual | *September 16, 1966 to March 15, 1967*

SENSITIVITY FUNDAMENTALS (U)

Prepared for:

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
WASHINGTON 25, D.C.

CONTRACT Nonr 3760(00)

S RI Project FRU-4051

Approved: N. K. HIESTER, DIRECTOR
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GROUP-4
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ABSTRACT

Low Velocity Detonations

(This section is unclassified)

The conventional gap test was used to investigate the importance of confinement material and geometry on the low velocity detonation (LVD) shock sensitivity of the difluoroamino compounds. Unusual results for 1,2-DP, summarized in this report, led to high speed framing camera studies of its LVD initiation. The photographs show that several initiation mechanisms influence the conventional gap test. These mechanisms are discussed in terms of confinement geometry and material as well as initial shock input.

A relationship between the LVD gap sensitivity and initial decomposition kinetics is also discussed.

Chemistry and Physics of Detonation

Concepts of transient detonation phenomena in the simple difluoroamino liquids underwent a change during the past six months. Adiabatic explosion theory is still basic for failure on liquids, but the concept apparently must be applied in a new way. Failure diameter studies on iBA and 2,3-DB have been completed, and the importance of dark waves in 1,2-DP has been partially elucidated. Reaction-time measurements on nitromethane have proved out suitable reaction chambers, demonstrated the effect of pressure profile on initiation behavior and indicated the necessity for careful temperature control. Final reaction-time measurements on 1,2-DP and IBA are in progress.

Kinetics of Decomposition of NF Compounds in Aqueous Solution

In the kinetic studies of dehydrofluorination of NF compounds in aqueous solution, rates and activation parameters have now been determined for 1,3-DP, 1,2,2-TP, and 2,2,3-TB in 30% diglyme-70% water between 50°

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and 75°C. To date, eight bis and tris propanes and butanes have been examined. Studies have also been initiated on the photolysis of NF compounds. Preliminary results for t-BD are available.

Very Low Pressure Pyrolysis (VLPP)

A detailed kinetic study of the decomposition of t-butyl difluoramine via VLPP has been carried out. The decomposition yields, as major products, N_2F_4 and $(CH_3)_2C=CH_2$; a minor product is $(CH_3)_3CH$. We conclude from the study that the pyrolysis proceeds through homolysis of the C-N bond and follows the rate law

$$k = 10^{16.6 \pm 0.2} \left(\exp - \frac{(60 \pm 1) \times 10^3}{RT} \right)$$

Inspection of the summary of VLPP data for the compounds 2,2-DP, IBA, 1,1-DP, 1,2-DP, and t-BuNF$_2$ allows us to conclude that the C-N bond in an alkyl difluoroamino compound is weakened both by replacement of hydrogen by carbon on the NF$_2$-bearing carbon and by a close proximity of NF$_2$ groups within the same molecule.

A chemical model involving chain processes for detonation propagation is proposed to explain failure diameter differences between geminal and nongeminal NF compounds. It is suggested that detonation propagation in the nongeminal compounds proceeds by means of a chain with fluorine atoms as chain carrier, and that detonation in the geminal compounds proceeds via a chain with both F and NF$_2$ as chain carriers.

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FOREWORD

This project is the responsibility of the Industrial Sciences Laboratory in cooperation with the Poulter Research Laboratories and the Chemical Physics Division. Project organization and principal contributors to the technical work follow:

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GLOSSARY OF COMPOUNDS

Code Name	Structure	Chemical Name
2,3-BIB	$CH_3-\underset{NF}{\overset{\|}{C}} - \underset{NF}{\overset{\|}{C}}-CH_3$	2,3-bis(fluorimino)butane, geometric isomers
t-BD	$(CH_3)_3CNF_2$	t-butyl difluoroamine
2,3-DB-1, -2	$CH_3-\underset{NF_2}{\overset{\|}{CH}} - \underset{NF_2}{\overset{\|}{CH}}-CH_3$	2,3-bis(difluoroamino)butanes, diastereoisomers
DDP	$CH_3\underset{NF_2}{\overset{\overset{NF_2}{\|}}{C}}-CN$	2,2-bis(difluoroamino)propionitrile
DIN	$CH_3-\underset{CH_3}{\overset{\overset{NF_2}{\|}}{C}}-CN$	2-difluoroamino-2-methylpropionitrile
1,1-DP	$CH_3CH_2\underset{NF_2}{\overset{\overset{NF_2}{\|}}{CH}}$	1,1-bis(difluoroamino)propane
1,2-DP	$CH_3-\underset{NF_2}{\overset{\|}{CH}}-CH_2-NF_2$	1,2-bis(difluoroamino)propane
1,3-DP	$F_2NCH_2CH_2CH_2NF_2$	1,3-bis(difluoroamino)propane
2,2-DP	$CH_3C(NF_2)_2CH_2$	2,2-bis(difluoroamino)propane
FDB	$CH_3-\underset{NF_2}{\overset{\overset{NF_2}{\|}}{C}} - \underset{}{\overset{\overset{NF}{\|\|}}{C}}-CH_3$	2,2-bis(difluoroamino)-2-fluorimino-butane
IBA	$CH_3-\underset{CH_3}{\overset{\overset{NF_2}{\|}}{C}} - CH_2NF_2$	1,2-bis(difluoroamino)-2-methyl propane
1-MB	$CH_3CH_2CH_2CH_2NF_2$	1-difluoroaminobutane
2-MB	$CH_3CH_2CH(NF_2)CH_3$	2-difluoroaminobutane
NFP	$CH_3-\underset{NF}{\overset{\|\|}{C}}-C\equiv N$	N-fluoriminopropionitrile
2,2,3-TB	$CH_3-\underset{NF_2}{\overset{\overset{NF_2}{\|}}{C}} - \overset{\overset{NF_2}{\|}}{CH}CH_3$	2,2,3-tris(difluoroamino)butane

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Code Name	Structure	Chemical Name
TMEA	$CH_3-\overset{\displaystyle NF_2}{\underset{\displaystyle CH_3}{C}} - \overset{\displaystyle NF_2}{CH} - CH_3$	2.3-bis(difluoroamino)-2-methyl-butane (trimethylethylene adduct)
1,2,2-TP	$CH_3-\overset{\displaystyle NF_2}{\underset{\displaystyle NF_2}{C}} - CH_2NF_2$	1,2,2-tris(difluoroamino)propane

I   INTRODUCTION

Under the sponsorship of the Office of Naval Research, Stanford Research Institute is studying fundamental sensitivity properties of difluoroamino compounds in the following situations:

1. The low velocity reaction wave characteristics of the liquid phase.

2. The relation of shock sensitivity and failure diameter to the flow and the chemical reaction rate behind the shock front.

3. The mechanism and kinetics of thermal decomposition of the compounds in solution and in the gas phase.

The detonation studies described in this report include recent results obtained in the study of low velocity detonation (LVD) waves in difluoroamino compounds. Previously, low velocity waves were reported[1] in lead confinement at characteristic diameters below the failure diameter of a high velocity wave. The purpose of this task during this report period was to determine if the phenomenon is general under conditions of larger diameter and different materials of confinement, and to relate the LVD to chemical decomposition mechanisms (Section II).

The ultimate objective of studies of the physics and chemistry of detonation (Item 2 above) is to correlate transient detonation phenomena, such as shock initiation and failure behavior, with decomposition kinetics. This objective involves: (a) measurement of failure diameters; (b) study of events in the liquids as shocks of various magnitudes enter; and (c) measurement of reaction times at pressures and temperatures comparable to those encountered in initiating shocks. During the past six months, effort has been partly devoted to continued study of the failure diameter of difluoroamino compounds, to diagnostic experiments on dark waves, and to an effort to determine whether dark waves enter into the mechanism of failure for the DP isomers. Reaction time measurements made in shocked difluoroamino compounds have received considerable emphasis; these measurements are pertinent to failure diameter theory, dark waves, and high temperature chemical kinetics in the liquid phase.

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Sections IV and V of this report describe a study of the decomposition behavior of NF compounds in solution at low temperature and in the gas phase at low pressure and high temperature. The first study particularly relates to the chemical reactivity of difluoroamino compounds, giving pertinent information on the effect of environmental factors such as container materials and presence of catalytic impurities. From the latter study, knowledge of the thermal stability of simple difluoroamino groupings and of the initial bond breaking reaction and bond energies is being derived. Most recently emphasis has been given to obtaining knowledge of the first few steps of decomposition and correlating these with the low velocity detonation phenomena.

The compounds chosen for this study are as simple as possible structurally but at the same time they have physical properties that permit their use in each phase of the study. The model compounds are the bis difluoroamino and tris difluoroamino isomers of the propane series--primarily 1,2-, 1,3-, 1,1-, and 2,2-bis(difluoroamino)propane (1,2-, 1,3-, 1,1-, and 2,2-DP); 1,2-bis(difluoroamino)-2-methyl propane (IBA); 2,3-bis(difluoroamino)butane, (2,3-DB) in meso and <u>d</u>, <u>1</u> forms; 1,2,2-tris(difluoroamino)propane (1,2,2-TP); and 2,3,3-tris(difluoroamino)butane (2,3,3-TB). These compounds are being used so that the results from each experimental technique can be interrelated without having to account for effects caused by different functional groups, amount of carbon content, and chain branching. Through the use of isomers, structural effects on the results from a particular technique can be determined-- for example, the differences in the effect of vicinal and geminate difluoroamino groups on the ease of initiation and on the environmental stability of compounds containing them.

References

1. Stanford Research Institute, Project 4051, Technical Progress Report 66-2 (Annual), "Sensitivity Fundamentals," March, 1966, <u>et seq.</u>

II   LOW VELOCITY DETONATIONS

(A.B. Amster and R.W. Woolfolk)

A.   Introduction

Low velocity detonation (LVD) here denotes a reaction wave that propagates supersonically, but at velocities below those predicted by hydrodynamic considerations. We have proposed a model for LVD which predicts that the gap sensitivity will depend on the geometry and material of confinement. During this report period our studies of LVD sensitivity in the difluoroamino compounds emphasized these effects of container material and geometry. In the course of conducting sensitivity tests anomalous   results   led   to some exceedingly interesting and revealing high speed framing camera studies which we will describe and discuss.

Also, a recently noted connection between the LVD gap sensitivity of 1,2-DP and 2,2-DP and their initial decomposition kinetics will be discussed in light of the new developments concerning the gap sensitivity test.

B.   Theoretical Considerations

In 1965[1] we proposed a physical model for the initiation and propagation of LVD. This model, further refined in subsequent work[2,3] involves the Mach interaction within shocked liquids confined in high sonic velocity materials. When a plane shock wave impinges upon a liquid with a sonic velocity lower than that of its confinement material, either of the situations depicted in Fig. 1 occur. In rectangular geometry either Mach or regular reflection can occur, but in cylindrical geometry a Mach interaction always occurs.[4,5] The pressure and temperature behind the Mach zone are quite high. (See Ref. 2 for a detailed discussion of the theory and calculation of pressures and temperatures in cylindrically confined water.) We believe that this Mach interaction is responsible for some kinds of LVD initiation and contributes to propagation. Photographic studies using mixtures of tetranitromethane (TNM) and nitromethane (NM) have shown that the Mach zone is probably present in liquids undergoing LVD.[3]

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(a) REGULAR REFLECTION   (b) MACH REFLECTION   TA-4051-50
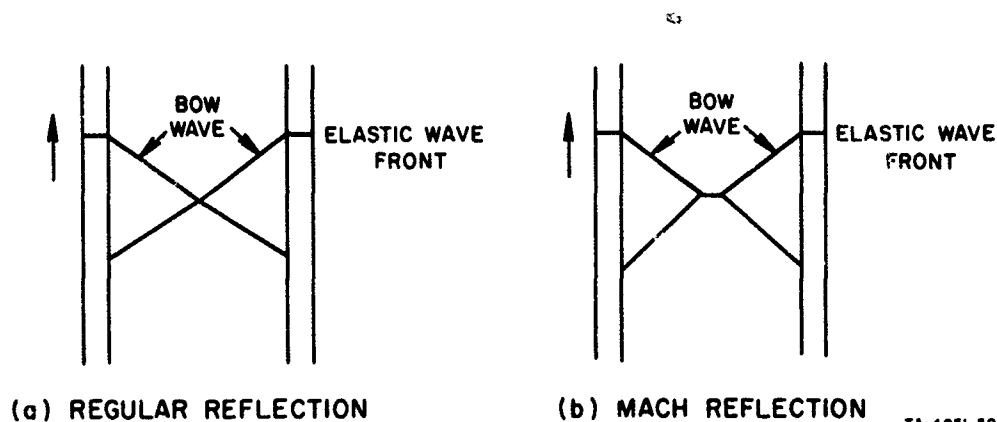
FIG. 1 SHOCK WAVE INTERACTIONS IN FLUIDS CONTAINED IN WALL MATERIAL
OF HIGH SONIC VELOCITY (U)

Recently we have become aware of some independent Russian work that
further confirms our Mach zone model.[6] Because of its importance a brief
description of this work is in order. Dimza's experiments consisted of
initiation of an explosive (TNM/toluene) confined in cylindrical tubes
of different sonic velocities. The confined explosive was placed in a
water-filled steel container. By varying the placement distance of an
electric detonator, a gap test was conducted with the water acting as an
attenuator for the detonator's shock wave. The "50% point" distance for
detonation of the explosive was determined and compared to the sonic
velocity of the tube. In Fig. 2 (curve 1) a plot of the 50% point distance
versus the sonic velocity of the confinement material is a straight line.
This relationship demonstrates that sensitivity increases as the container
sonic velocity increases. When air is substituted for water another
mechanism is apparent in which the confinement is unimportant. These
results are shown in curve 2 of Fig. 2. The air shock and hot gases
following this shock initiate the explosive; in contrast, in the water
case a pure shock is responsible for initiation. If, however, the hot
gases are prevented from reaching the explosive surface (if a thin layer
of water is added to the surface of the charge), the container sonic
velocity again becomes important. Streak camera studies showed that when

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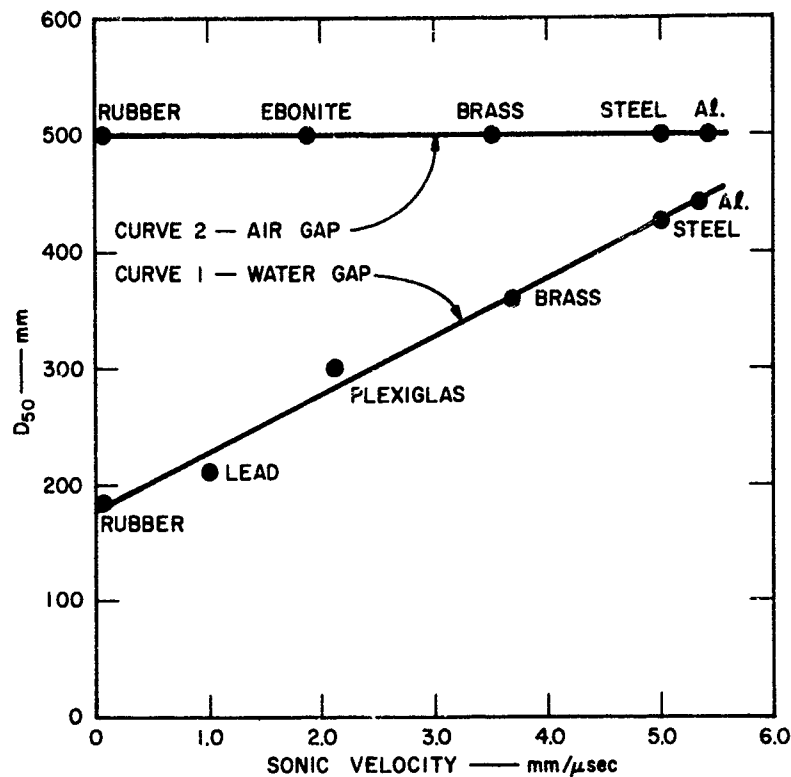
FIG. 2 50% POINT vs. CONFINEMENT SONIC VELOCITY
FOR TNM/TOLUENE (U)

the confinement material was controlling, the initiation occurred deep in the center of the cylindrical charge.[*] The uncovered air shots initiated at the surface. Dimza concluded ".... that two firing mechanisms are present: (a) direct firing by hot gases at the surfaces ....; (b) firing by a shock wave propagating across the charge when the casing itself takes a major part in the initiation of the detonation." Our experimental program has led us toward a similar conclusion. We are also studying the effects of rectangular and cylindrical geometry.

C.   Experimental Program

A substantial number of gap sensitivity tests[7] have been conducted with 1,2-DP. Figure 3 is a schematic diagram of the test arrangement and Fig. 4 is a photograph of the experimental arrangement for very large gaps.

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[*]This corresponds to the region of the Mach zone, in our model, a phenomenon Dimza did not discuss.

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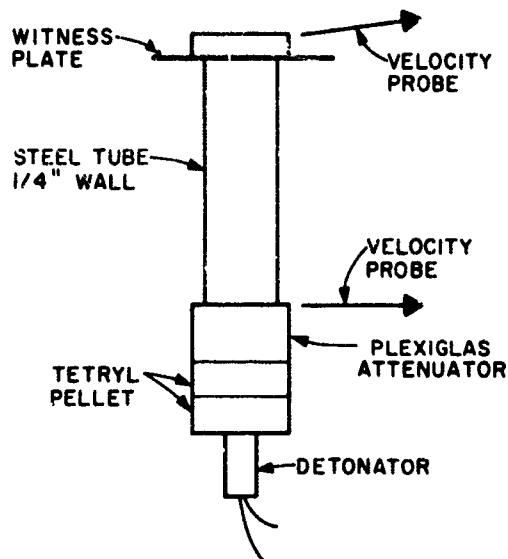
FIG. 3 LVD GAP TEST ARRANGEMENT (U)

The results of the LVD gap tests for 1,2-DP are summarized in Table I. The average velocities are somewhat erratic and are especially suspect when they are subsonic ($< \sim 1.2$ mm/μsec). As a check on our method of determining LVD gap sensitivity a TNM/NM mixture (18.7% TNM) was tested with the results shown in Table II.

The results with lead tubes (Table I) were not in accord with our theory that low sonic velocity confinement should not initiate LVD because no Mach interaction is possible. This discrepancy prompted a framing camera study of the gap sensitivity test using a shadowgraphic lighting technique with an electronic flash at the focus of a Fresnel lens. Figures 6 and 7 each show eight selected frames from a 25-frame sequence of 1,2-DP initiated in lead tubes at a gap of 30.5 cm. The results in Fig. 6 were obtained without a witness plate; for those in Fig. 7 a witness plate was used. These frames show clearly (at least the negatives) that initiation is caused not by the initial shock but at a substantially later time by

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WITNESS PLATE
AND SAMPLE TUBE

PLEXIGLAS
ROD (GAP)

TETRYL

FIG. 4   187 cm   GAP   TEST   SETUP   (U)

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Table I

GAP SENSITIVITY OF 1,2-DP*

Material (Sonic Velocity)	Aluminum (5.1 mm/μsec)		Steel (5.0 mm/μsec)	Brass (3.7 mm/μsec)	Lead (1.2 mm/μsec)
Geometry (I.D. cm)	Round (1.27)	Square (1.27 x 1.27)	Round (1.27)	Round (1.27)	Round (1.27)
Wall Thickness (cm)	0.23	0.318	0.635	0.23	0.635
Temperature (°C)	12 ± 1	9 ± 1	16 ± 2	10 ± 2	10 ± 1
Gap (cm Plexiglas)					
3.81			+2.9		
5.08			+		
7.62			+		
10.2					+0.85**
24.8			+1.8		
30.5			+2.3		+0.87**
34.3	+4.5	+3.5			
61.0		+1.9			
61.0		+			
64.8			+2.7		
91.5		–		+ 1.3	+0.63**
91.5		–		+~1.2	–(rubber witness)
95.4			?***		
122				+ 1.3	
122				?***	
126			–		
153	+1.2**		–		
183	+0.89**				
187			–		
214	+0.90**			–	

* + indicates detonation numbers are average velocity in mm/μsec; – indicates no detonation.

** Low average velocity may indicate delayed reaction.

*** ? indicates evidence of partial damage only.

Table II

TNM/NM LVD GAP SENSITIVITY

Temperature 12 ± 1°C		
Confinement: Steel tube 1.27 cm I.D., 0.63 cm wall, 10.4 cm length, sonic velocity 5.0 mm/μsec		
Gap (cm Plexiglas)	Average Velocity (mm/μsec)	Witness Plate (+ = go, - = no go)
8.9	1.86*	+
10.2	----	-
11.4	----	-
16.5	----	-
30.5	----	-

*Bureau of Mines[8] reports 50% point = 11.0 cm and average velocity 2.2 mm/μsec at 20°C with 2.54 cm I.D., 0.635 cm wall, steel tube.

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the air shock from the donor tetryl explosive. The significant effects of the initial shock are to expand the lead tube (Frame 158 et seq.) and, presumably, to sensitize the liquid to the subsequent air shock. For comparison, Fig. 8 shows a shot performed under conditions identical to those used for that shown in Fig. 7 but with chloroform substituted for the 1,2-DP. The sequence of events before the arrival of the air shock is identical. Also, in Fig. 8 the initial shock in Plexiglas can be seen (again by careful examination of the negatives) because a polished square Plexiglas piece was placed at the end of the gap section. The velocity of the shock in the Plexiglas ($\sim$ 2.5 mm/μsec) agrees with that obtained by taking the slope of a curve of distance versus transit time for tetryl-loaded Plexiglas (Fig. 5).

A framing camera study of the gap test with 1,2-DP in other confinements was undertaken to ascertain if air shock is generally important in LVD initiation. Figures 9 and 10 are framing camera sequences of the gap test in steel confinement. Without a witness plate (Fig. 9) no reaction occurred and the tube was recovered with evidence that unreacted liquid was present. With a witness plate (Fig. 10), evidence of an explosive reaction is seen about 33 μsec after the arrival of the shock at the Plexiglas-steel interface. (The shock arrival time of 248 μsec is accurate only to about 5 μsec.) Thirty-three μsec is approximately the time required for a shock to travel up the steel wall, reflect, and return (i.e., 208 mm/$\sim$ 5.2 mm/μsec $\approx$ 40 μsec). This time coincides with the fragmentation of the Plexiglas from the increased shock pressure as shown in the 281 μsec frame of Fig. 10.

The 1,2-DP test results with aluminum tubes at a gap of 91.0 cm are shown in Figs. 11 and 12. The results are similar to those for steel confinement. The presence of a witness plate (Fig. 12) caused LVD detonation, but at a much slower rate than in steel tubes. Without a witness plate (Fig. 11) there was no evidence of reaction and the tube was recovered intact.

In the aluminum and steel tube tests there was no evidence of the air shock initiation seen in lead tube tests. One should note that in these instances neither the steel nor the aluminum tubes were recovered deformed. This is in contrast to the lead, which always was expanded, even when inert ingredients were tested. This is additional evidence that the expansion is a necessary precursor to air shock initiation.

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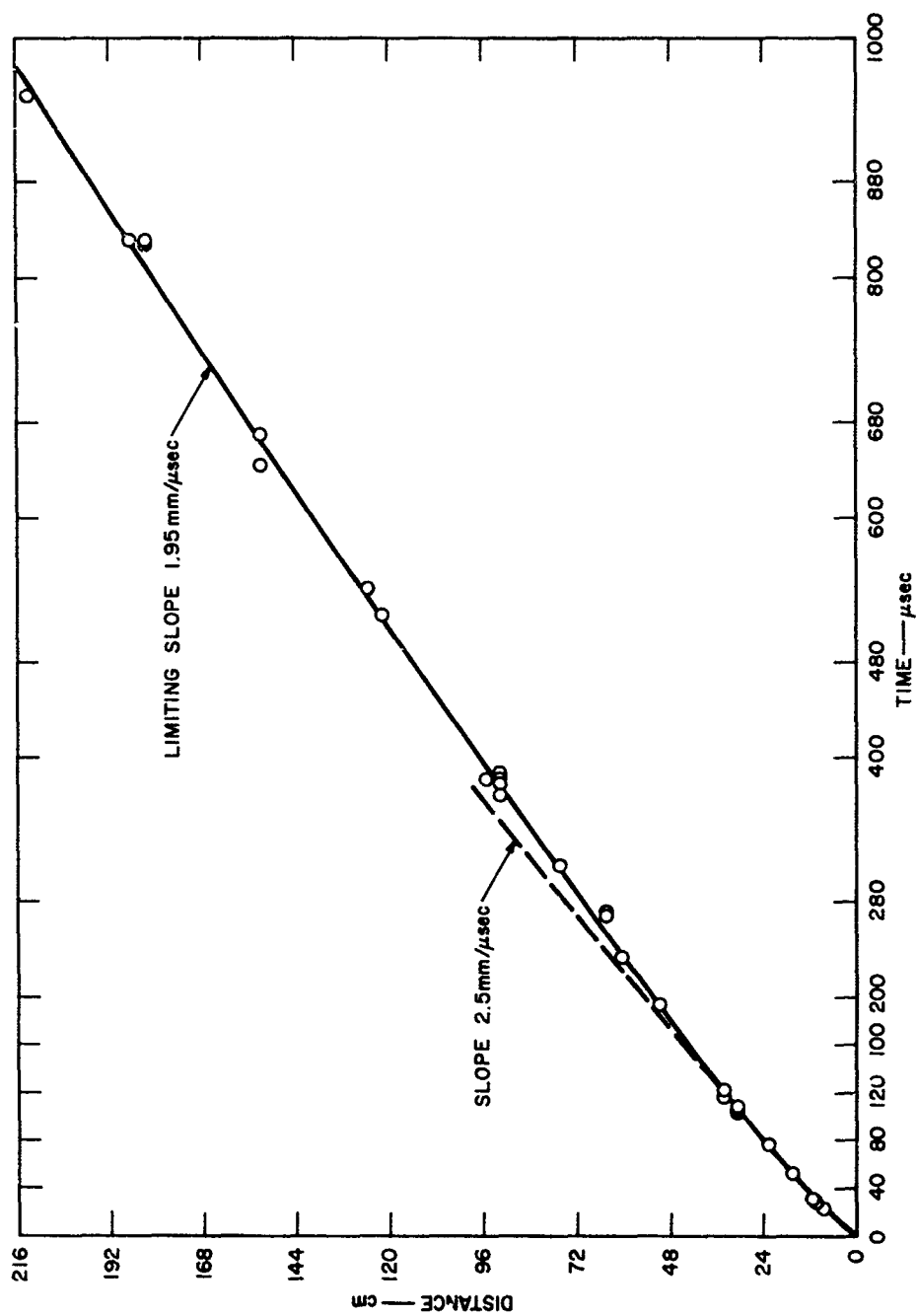
FIG. 5 TRANSIT TIME FOR SHOCK IN PLEXIGLAS (U)

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Figure 6

FRAMING CAMERA PHOTOS OF GAP TEST
IN LEAD CONFINEMENT WITHOUT WITNESS PLATE

(Donor detonated at time zero; gap 30.5 cm)

Time (μsec)	Remarks
142	Shock arrives at 120 μsec
167	Tube starts to expand (arrow)
217	Air shock apparent (arrow) and tube continues expansion and movement away from Plexiglas
250	Air shock approaching expanding tube (arrow)
267	Air shock arrives at expanded tube end (arrow)
275	Detonation starts as air shock crosses expanded end of tube
292	Detonation under way; note unreacted liquid leaving tube (arrow)
325	Detonation arrives at the top of the tube (arrow)
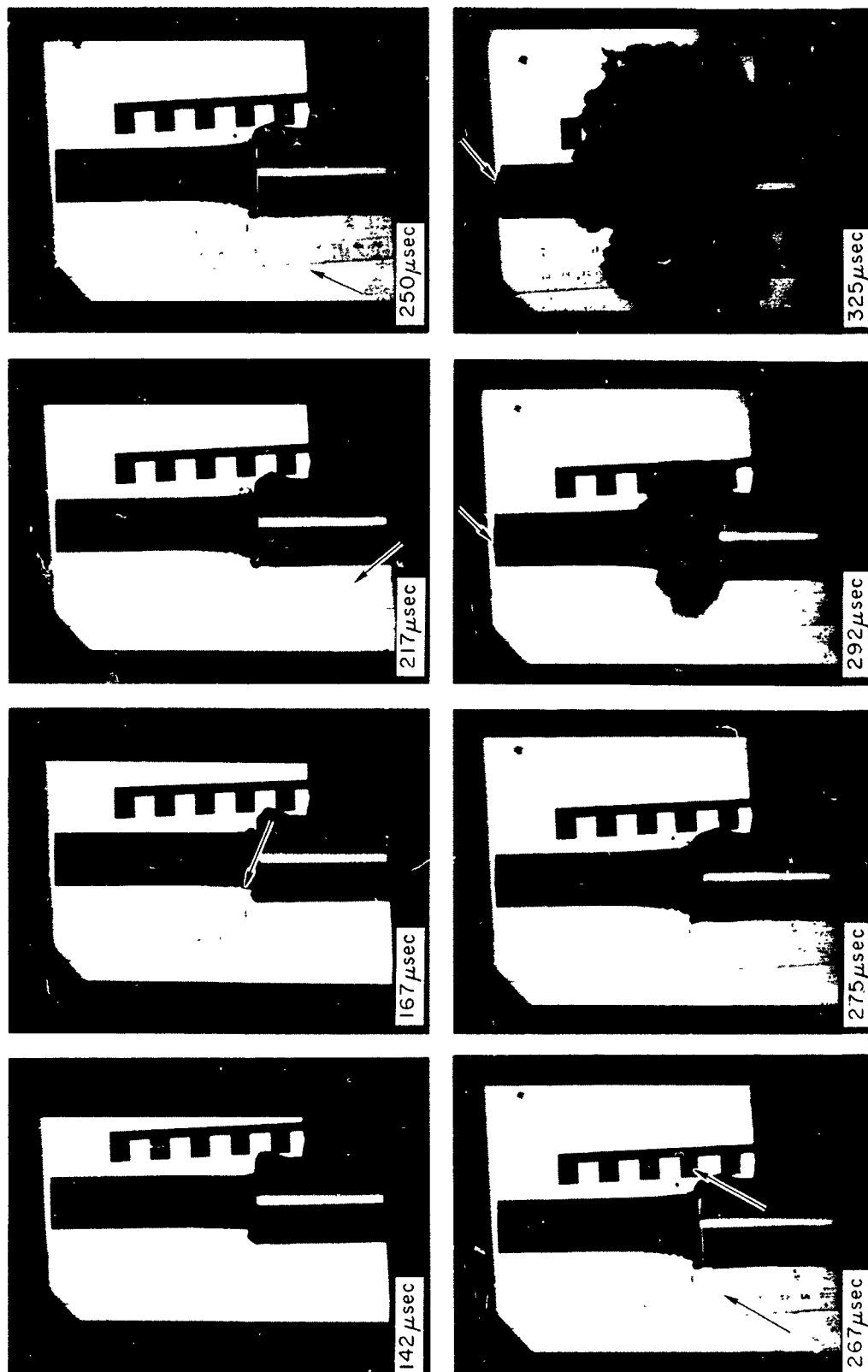
FIG. 6 FRAMING CAMERA PHOTOS OF GAP TEST IN LEAD CONFINEMENT WITHOUT WITNESS PLATE (U)

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Figure 7

FRAMING CAMERA PHOTOS OF GAP TEST
IN LEAD CONFINEMENT WITH WITNESS PLATE

(Donor detonated at time zero; gap 30.5 cm)

Time (μsec)	Remarks
122	Shock arrival
147	Tube starting to expand (arrow)
205	Expansion continues also air shock appears (arrow)
238	Tube expands and moves away from Plexi-glas (arrow) and air shock moves toward tube (arrow)
271	Air shock reaches expanded tube (arrow)
279	Detonation begins
296	Detonation continues
313	Full-scale detonation
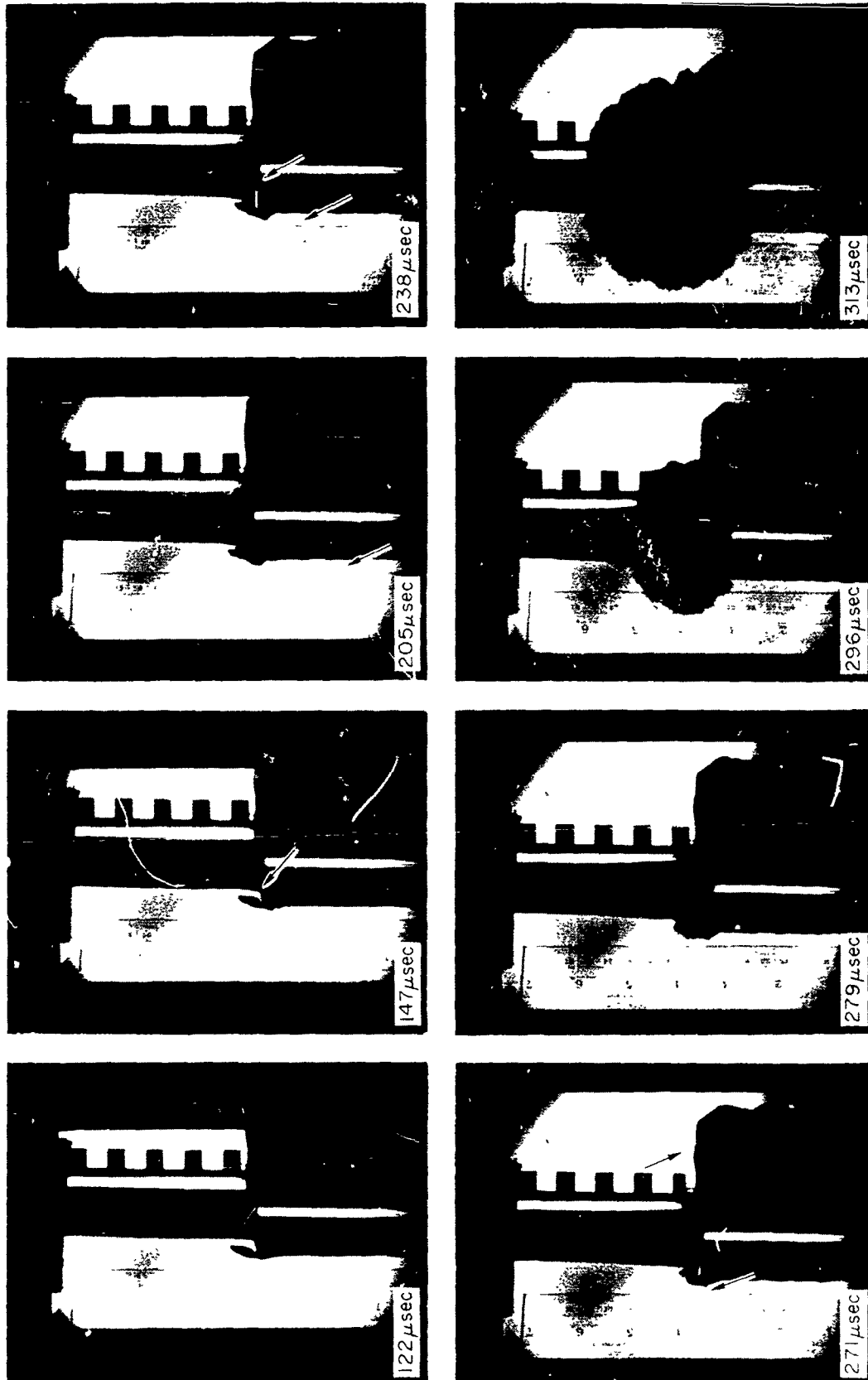
14

FIG. 7 FRAMING CAMERA PHOTOS OF GAP TEST IN LEAD CONFINEMENT WITH WITNESS PLATE (U)

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Figure 8

FRAMING CAMERA PHOTOS OF INERT GAP
TEST IN LEAD CONFINEMENT

(Donor detonated at time zero; gap 30.5 cm)

Time (μsec)	Remarks
98	Plexiglas shock (arrow)
116	Shock arrival
141	Shock reflected at boundary (arrow)
158	Tube begins to expand
¹99	Tube continues to expand and an air shock is visible (arrow)
257, 265	Strong air shock (arrow)
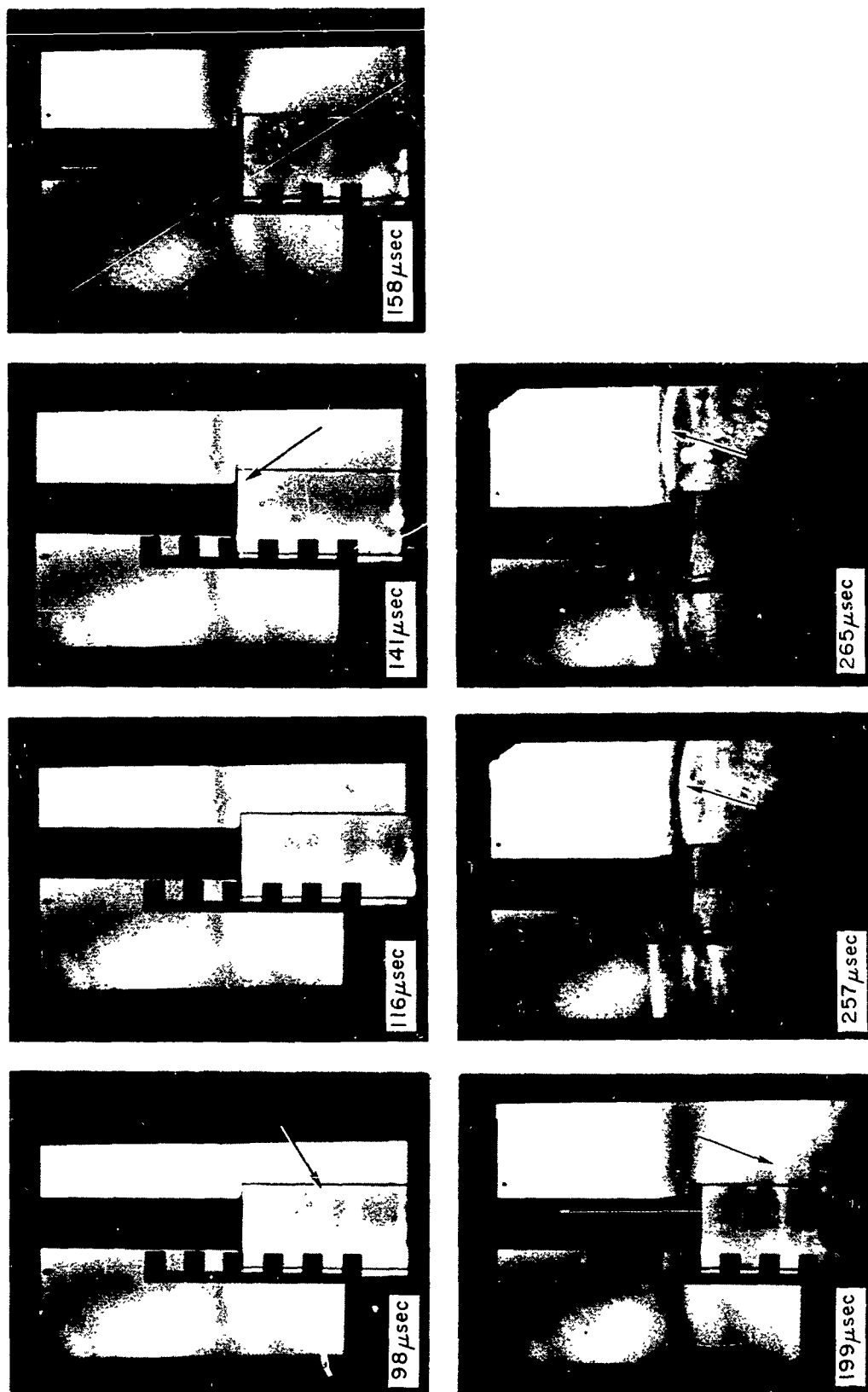
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FIG. 8 FRAMING CAMERA PHOTOS OF INERT GAP TEST IN LEAD CONFINEMENT (U)

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Figure 9

FRAMING CAMERA PHOTOS OF GAP TEST
IN STEEL CONFINEMENT WITHOUT WITNESS PLATE

(Donor detonated at time zero; gap 61.0 cm)

Time (μsec)	Remarks
219	Before shock arrival
244	Shock arrives at 248 μsec
286	Reflected shock returns and Plexiglas begins breaking up (arrow)
311	Plexiglas continues to break up (arrow)
336	Plexiglas breaking up; no evidence of explosive reaction
386	No evidence of reaction
403	No evidence of reaction; also note liquid spray at top of tube (arrow)
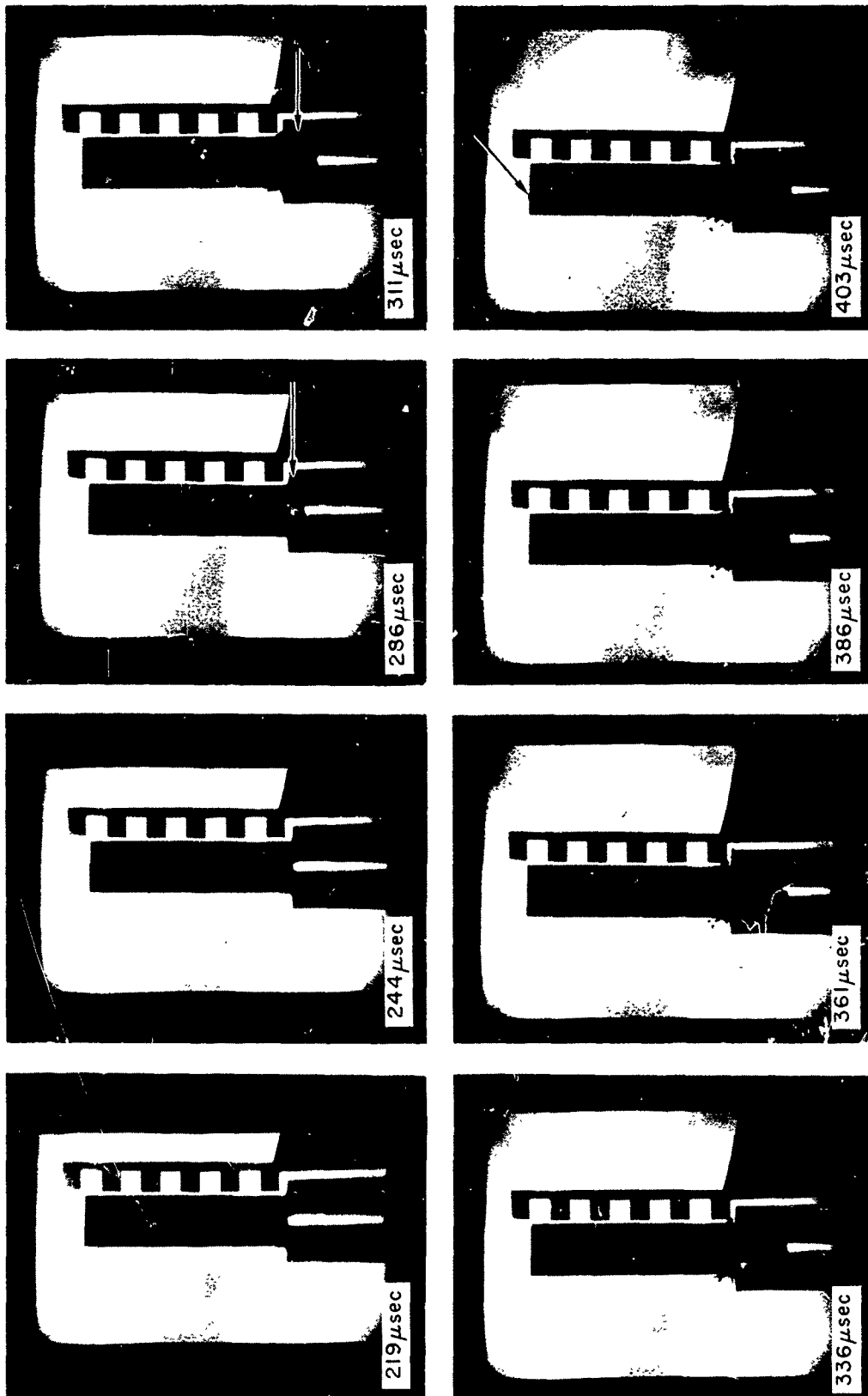
FIG. 9 FRAMING CAMERA PHOTOS OF GAP TEST IN STEEL CONFINEMENT WITHOUT WITNESS PLATE (U)

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Figure 10

FRAMING CAMERA PHOTOS OF GAP TEST
IN STEEL CONFINEMENT WITH WITNESS PLATE

(Donor detonated at time zero; gap 61.0 cm)

Time (μsec)	Remarks
231	Before shock arrival
248	Shock arrival
281	First signs of detonation; also cracking of Plexiglas (arrows)
306	Witness plate begins to swell
331	Witness plate swelling
348	First signs of reaction at witness plate (arrow)
356	Reaction breaking through witness plate (arrow)
373	Full-scale detonation
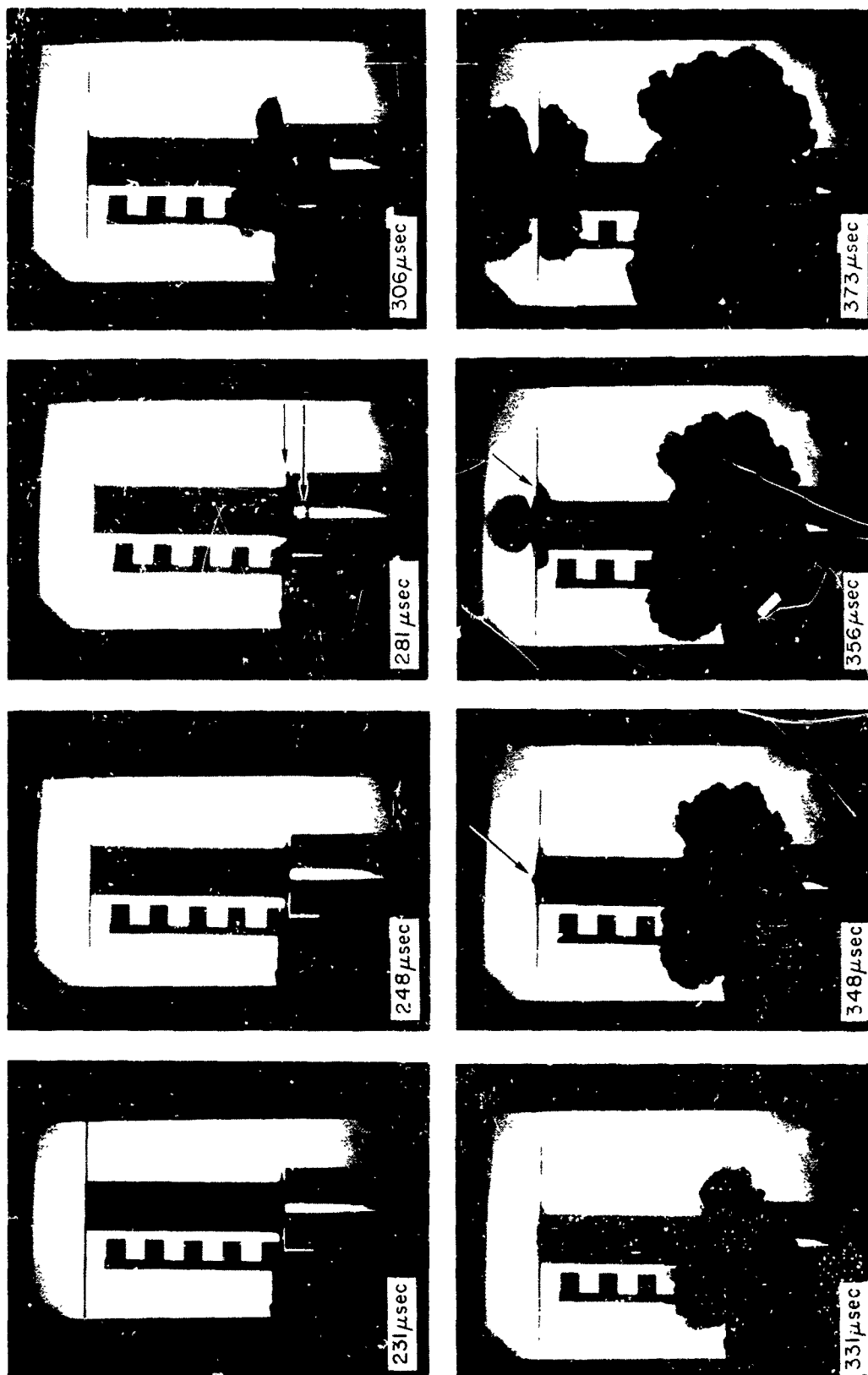
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FIG. 10 FRAMING CAMERA PHOTOS OF GAP TEST IN STEEL CONFINEMENT WITH WITNESS PLATE (U)

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Figure 11

FRAMING CAMERA SEQUENCE OF GAP TEST
IN ALUMINUM CONFINEMENT WITHOUT WITNESS PLATE

(Donor detonated at time zero; gap 91.5 cm)

Time (μsec)	Remarks
360	Before shock arrival
393	Shock arrives at Plexiglas-tube interface
410	Gap closes between marker and Plexiglas interface (arrows)
435	Note marker bending
460	Marker continues to bend and tube begins to lift from surface
485	Tube continues to lift (arrow)
510	Marker continues to bend and tube begins to leave surface
535	Tube leaves surface; no evidence of reaction (arrow)
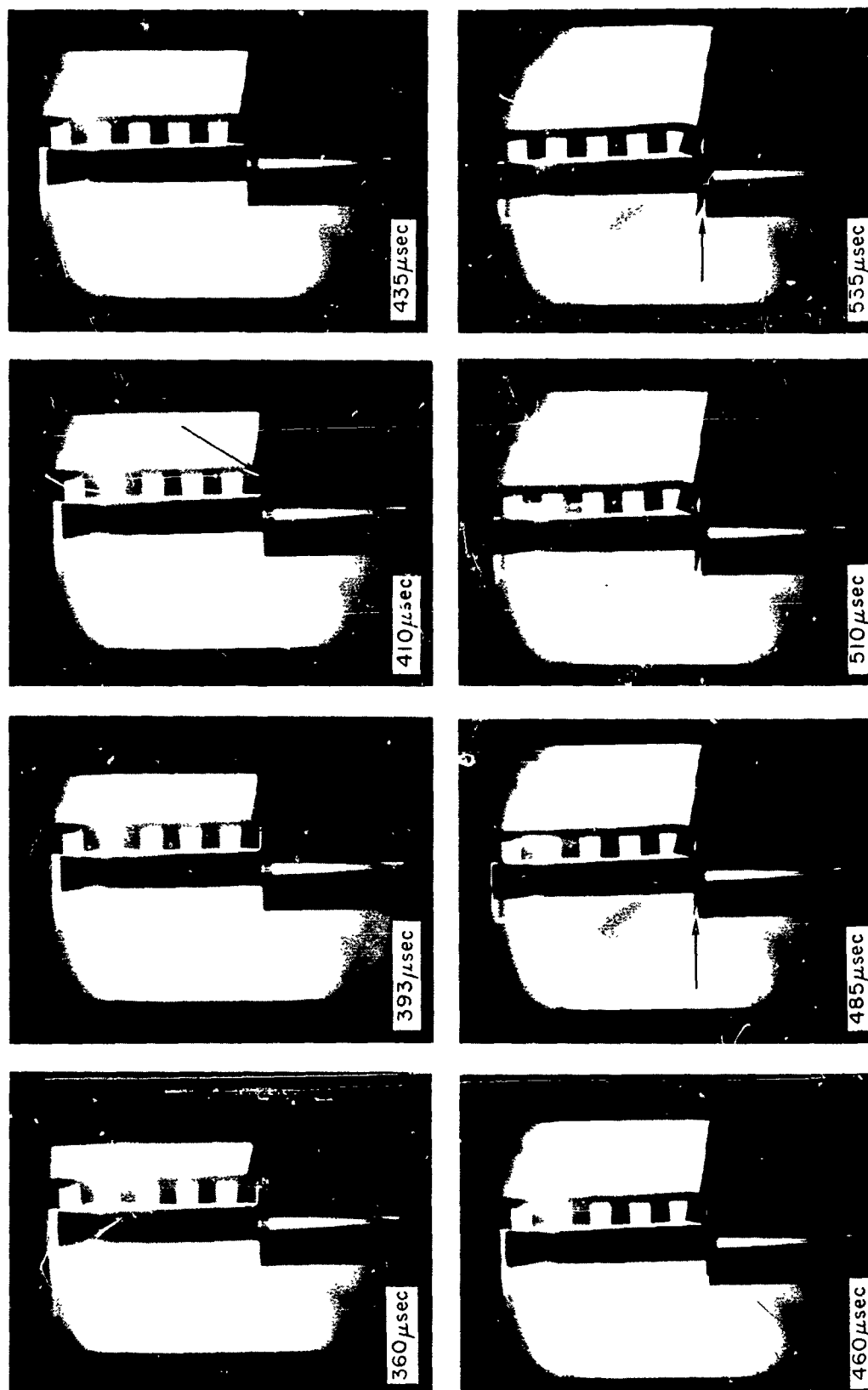
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FIG. 11 FRAMING CAMERA SEQUENCE OF GAP TEST IN ALUMINUM CONFINEMENT WITHOUT WITNESS PLATE (U)

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Figure 12

FRAMING CAMERA SEQUENCE OF GAP TEST
IN ALUMINUM CONFINEMENT WITH WITNESS PLATE

(Donor detonated at time zero; gap 91.5 cm)

Time (μsec)	Remarks
360	Before shock arrival
393	Shock arrival
410	Marker gap closes (arrow)
435	First evidence of reaction at top of witness plate
460	Witness plate begins to swell (arrow)
485, 510, 535	Note witness plate swelling, marker bending from shock force, and tube lifting from surface (arrows)
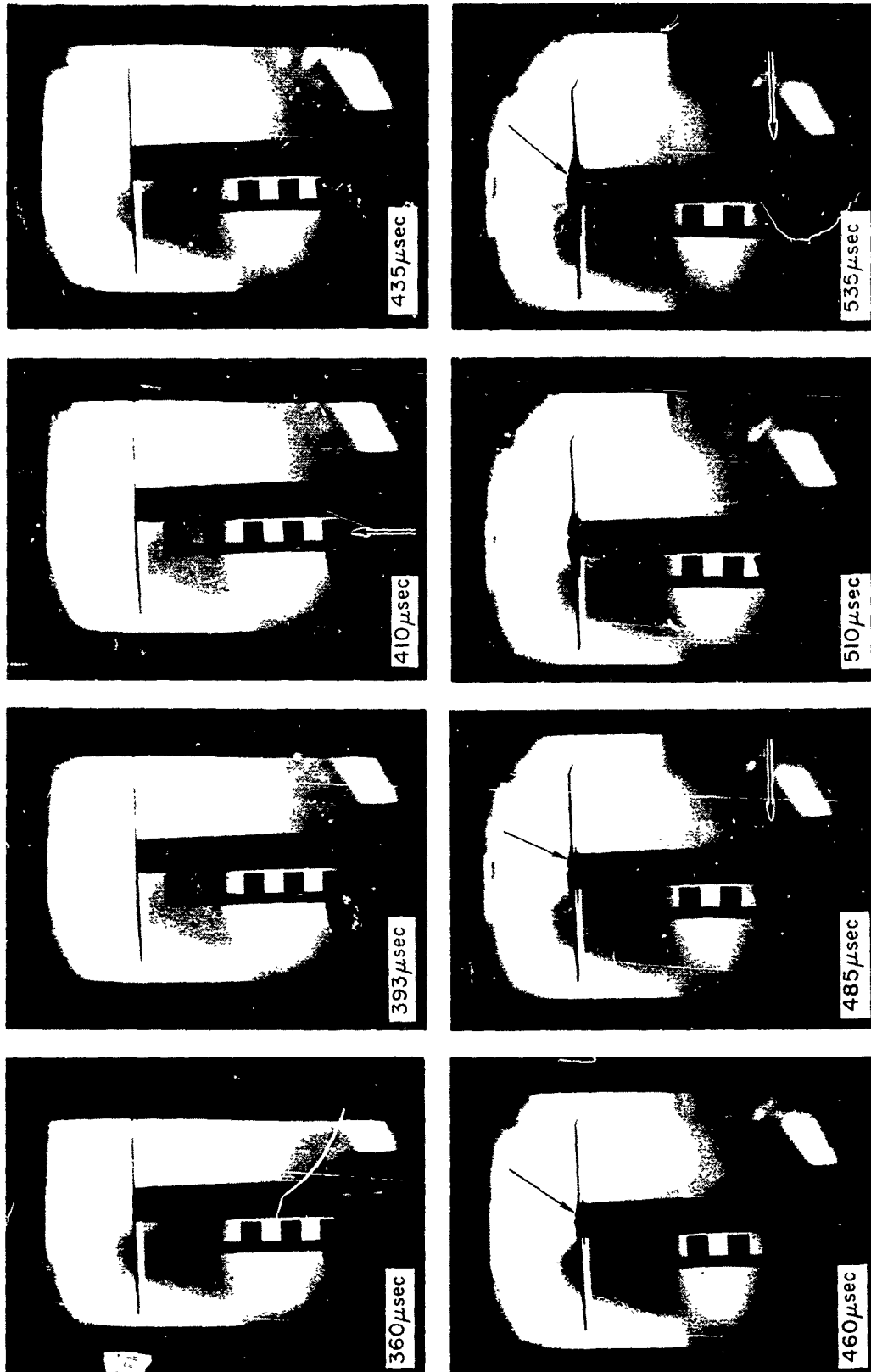
24

FIG. 12 FRAMING CAMERA SEQUENCE OF GAP TEST IN ALUMINUM CONFINEMENT WITH WITNESS PLATE (U)

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D. Discussion

The average velocities of LVD obtained i the gap test experiments may have very little meaning because initiation evidently does not always occur immediately. The placing of probes in the liquid to obtain velocity readings is of doubtful usefulness because they can reflect the initial shock and act as reaction sites. We have attempted to use pressure probes placed flush with the container walls, but have met with little success. We are still hoping to find a reliable velocity measuring device that will not adversely affect the results.

However, some comparisons are possible for systems that are similar (i.e., where only one variable--material, geometry, etc.--is changed). The difference made by the use of rectangular rather than cylindrical geometry is shown in Table I. In round aluminum tubes 1,2-DP is initiated even after 214 cm of attenuation, whereas in rectangular aluminum tubes initiation occurs only at less than 91.5 cm. This general behavior is in accord with our Mach zone theory. When only the confinement material is changed, as with the round aluminum and brass tubes, initiation is easier in higher sonic velocity materials. Dimza[6] has drawn the same conclusions. The steel tubes are excluded from these comparisons because their greater wall thickness may have an effect still to be investigated. Because of the different initiation mechanism in lead tubes these results also are not comparable with the others.

LVD gap sensitivity results obtained for 1,2-DP and 2,2-DP under identical conditions show a relationship between their initial decomposition kinetics and their gap sensitivities. Table III summarizes this relationship. The results in Table III suggest that as the bond energy of the C-N bond (the initial decomposition step is the homolysis of the C-N bond) is decreased, the LVD gap sensitivity is increased. 1,2-DP and 2,2-DP are ideal compounds for this type of comparison because they differ only in the placement of the NF_2 group, and their thermodynamic properties are almost identical. For comparison, NM, which does not undergo LVD, was included. It failed to react in the VLPP reactor. This information is also consistent with some reported elsewhere.[9] IBA, whose $T_{\frac{1}{2}}$ is 650°K, will be tested to ascertain whether the

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Table III

RELATIONSHIPS OF INITIAL DECOMPOSITION KINETICS
AND LVD GAP SENSITIVITY

Compound	$T_{\frac{1}{2}}$, $°K^*$	LVD Gap Sensitivity (cm Plexiglas)
2,2-DP	575	> 187
1,2-DP	~ 740	> 91 - < 126
NM	>>1200[†]	(no LVD reaction)

$^*T_{\frac{1}{2}}$ is the temperature for 50% initial decomposition as determined by D. Ross (see Section V, and Ref. 10).

[†]No evidence of reaction in VLPP reactor at 1200°K.

relationship between initial decomposition kinetics and LVD gap sensitivity
is valid for other difluoroamino compounds.

E. Conclusions

On the basis of our work we tentatively draw the following conclusions
concerning LVD gap sensitivity tests:

1. At high shock pressures, initiation of high velocity
   detonation (HVD) occurs (for 1,2-DP the HVD 50% point
   is 1.5 cm of Plexiglas).

2. Mach zone interactions are important for an intermediate
   shock pressure type of explosive initiation in high sonic
   velocity confinement.

3. At very low shock pressures, a reinforcing wave can reflect
   from the conventional witness plate, and the resulting
   higher pressure will cause explosion.

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4. Under special circumstances the initial shock wave can cause expansion of the container; this leads to fragmentation and cavitation of the liquid. The liquid may then be initiated when the air shock from the donor collapses the cavities, causing rapid combustion and/or explosion.

For Case 3 the reflected shock wave from the witness plate will have its strongest effect on liquids which are confined in high sonic velocity material because of the Mach zone formation in the reflected wave. Therefore gap sensitivities will be different with and without a witness plate present in this type of confinement. We also conclude that the conventional gap sensitivity results have little meaning in terms of initial shock donor pressure for LVD because of the variety of initiation processes that can occur.

F. Future Work

Our immediate goal will be to complete a series of conventional gap sensitivity measurements with and without witness plates, using the framing camera to determine the extent of reaction. This series will cover the range from initiation of high velocity detonations to very low amplitude shock initiation of LVD. Such a series should give a clearer understanding of the whole problem of gap sensitivity testing. After completion of this series, gap testing in varying confinement geometries and materials will be continued, to confirm the Mach zone theory further and to help formulate some criteria for safer storage and handling of LVD-prone liquids.

We have prepared the apparatus for a series of streak camera studies of the Mach zone in difluoroamino compounds undergoing LVD; from these studies we hope to ascertain how the reaction front behaves as it travels along the charge. We will continue to search for a reliable method of obtaining LVD detonation velocities. These experiments will be checked with photographic studies of LVD propagation.

UNCLASSIFIED

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UNCLASSIFIED

III   CHEMISTRY AND PHYSICS OF DETONATION

(M.W. Evans, L.B. Seely, J.G. Berke, and D. Tegg)

A.   Introduction

During the past two years work on the chemistry and physics of detonation of the difluoroamino liquids has concerned the transient rather than the steady-state detonation properties. The steady-state properties of explosives in general are comparatively well understood. Therefore, after a brief program to confirm that steady-state detonations in the difluoroamino liquids exhibited the properties normally to be expected, attention has been confined to the transient regime, which is less well understood.

Shock initiation is one of the simpler detonation processes that can be classified as transient. In shock initiation, of course, the detonation is growing. On the other hand, failure is a process characteristic of a degrading wave. Thus shock sensitivity and failure diameter are measurable quantities characteristic of these two types of transient behavior. The two processes are believed to be capable of theoretical treatment; a valid relation between them can probably be established.

We have made the a priori assumption that the shock sensitivity and failure diameter of a liquid ultimately depend on the chemical kinetics of decomposition of the compound. From a very general point of view this seems reasonable for the transient states. In contrast, the steady state depends on the thermochemistry and is independent of the kinetics. It is also a common assumption that decomposition kinetics depend on molecular constitution. Undeniably, other factors may affect the reaction path, particularly in the liquid state. Nevertheless, differences in the transient detonation properties of two similar compounds should correspond to differences in their molecular structures.

Determination of failure diameters went forward rapidly last year and is now complete for all four DP compounds. Tests on IBA and 2,3-DB have also been completed. The remaining tasks are to determine failure diameters for 1,2-DB and 2,2-DB, the precise homologs of 1,2-DP and 2,2-DP.

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Gap test shock sensitivities were reported by Amster[1] for a number of difluoroamino liquids. Detailed studies of the shock initiation process are now being completed and will augment these data. Information on the reaction time in shocked liquids is expected to elucidate the initiation process and to be directly applicable to failure diameter theory.

B. The Theoretical Problem

The theory of adiabatic constant volume explosion is fundamental to our treatment of transient detonation phenomena. The rate of a first order reaction is

$$\frac{dn}{dt} = Z(1 - n)e^{-E_a/RT} \tag{1}$$

where n = fraction of material reacted

Z = frequency factor

E_a = activation energy

R = gas constant

T = temperature

t = time.

The liquid is compressed and heated by a shock to a temperature T_s, which is supposed to be high enough to cause a slow rate of reaction. The further heating of the liquid beyond T_s is proportional to the amount that has reacted. The temperature is thus given by

$$T = T_s + n \frac{Q}{\overline{C}_v} \tag{2}$$

where Q is the energy released in the reaction and $\overline{C}_v$ is the average specific heat between T_s and T.

Equation (1) can be integrated[2] after Eq. (2) has been inserted to give the time when $n \to 1/e$ Because of the exponential nature of the rate law the precise final integration limits have little influence on the time at which the reaction rate becomes very fast,

$$t_r = \frac{C_v RT_s^2}{ZE_a Q} e^{E_a/RT} \tag{3}$$

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In considering the reaction of shocked difluoroamino liquids it cannot be assumed that the reaction is simple or necessarily first order. However, it can be assumed that a rate process which is exponential in the temperature results in a definite reaction time. For a low enough temperature the rate will be extremely slow during an induction period and its results will be practically undetectable. The temperature and the rate are nevertheless increasing during the induction time and will produce a very rapid reaction after a lapse of time about equal to t_r.

In the failure diameter theory used on this project, the assumption of what amounts to a complete equation of state[3] permits calculation of the reaction time through the computed shock temperature and Eq. (3). At the same time the equation of state defines state parameters for all shocks that can take place in the unreacted liquid. It is thus possible to express the reaction time t_r as a single-valued function of the shock speed U_s. The relation is characteristic of the physical and chemical properties of the liquid.

Another relation between reaction time and wave velocity can be developed on the basis of diameter effect theory. The various diameter effect theories attempt to relate wave velocity to reaction time by means of reasonable assumptions. On this basis a series of curves is derived, each again giving t_r as a single-valued function of wave velocity. Each curve of the family corresponds to a particular value of charge diameter. For large diameters the curves derived from diameter effect theory intersect the characteristic (t_r, U_s) curve of the substance in two points, one of which corresponds to the stable detonation velocity for that diameter. However, below some diameter the diameter effect curves no longer intersect the characteristic curve. The diameter at which the two curves are tangent is the theoretical failure diameter.

There are, of course, some shortcomings in the theory. For instance, diameter effect theory, with assumptions intended to be valid at large diameters, is applied to the opposite extreme of the diameter scale, namely, to the smallest diameter at which a detonation can be expected to exist. One can hope, however, that such oversimplifications will not obscure the

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general pattern of failure diameter behavior. In any case, careful experimentation is expected to bypass some of the difficulties and to permit clarification of others. It is in this light that the experimental programs undertaken must be viewed.

At a very minimum, failure diameters must be determined. Furthermore, they must be determined under conditions suitable for application of the theory. In particular, we must assure ourselves that the general picture of the failure process corresponds to the real case.

The requirement in diameter effect theory for a complete equation of state cannot be met with any accuracy at the present time. Perhaps this difficulty can be avoided by direct measurement of the reaction time t_r in a shock of known pressure. If this can be done (even approximately) it will remove the necessity for calculating the shock temperature T_s. The Hugoniot relation for the liquid is sufficient to express wave velocity in terms of pressure.

In their own right, reaction times represent chemical kinetics data which apply to the special conditions achieved in shocked liquids. Regardless of their use in failure diameter theory they may be compared with other data on the chemical nature of these particular compounds.

Finally, the simple difluoroamino liquids chosen for this particular study facilitate theoretical shortcuts, since all the DP isomers and some of their exact homologs are available. For instance, it is quite satisfactory to assume that the isomers have the same equation of state. Additionally, it can reasonably be assumed that a DP compound and its exact homolog have the same initial decomposition kinetics. Meaningful comparisons can therefore be made without absolute information for either compound.

C. Failure Diameters of Difluoroamino Liquids

Failure diameters of the DP isomers and of IBA and 2,3-DB are shown in Fig. 13. The failure diameters were determined in heavy lead blocks. The points shown on this graph are limited to those believed to be valid for determination of the failure diameter; they do not include experiments necessary to determine the proper booster size, which were shown on the
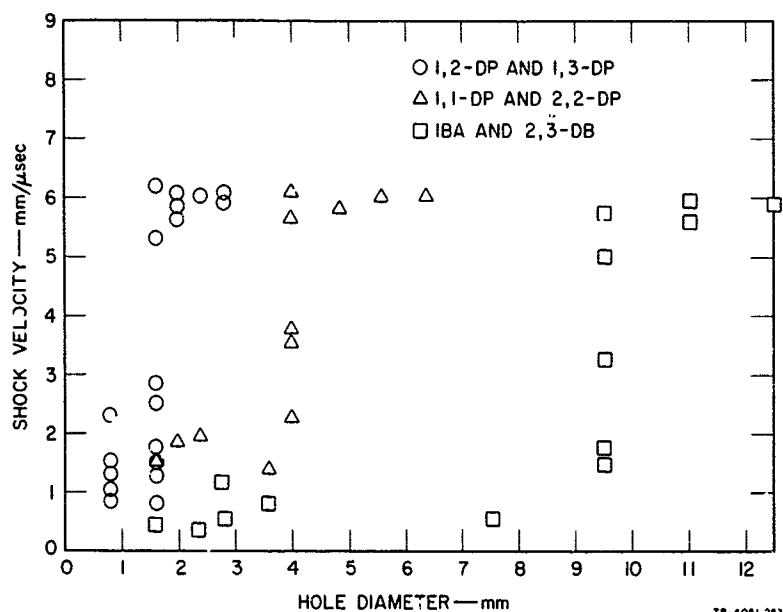
FIG. 13 FAILURE DIAMETER OF DIFLUOROAMINO PROPANE ISOMERS
AND TWO DIFLUOROAMINO BUTANES (The detonation velocities
of these compounds are near 6 mm/μsec; the change from low velocity
to this value indicates the approximate location of the failure diameter.) (C)

more detailed graphs published previously.[1] The values of shock velocity
are the average velocities calculated from the transit time of the wave
over the length of the block. The high values clustered near 6 mm/μsec
correspond well with the full-strength detonation velocity measured for
1,2-DP.

The graph establishes quite a clear difference between the failure
diameters of the geminate difluoroamino propanes and the nongeminate
isomers and thus provides a good example of the effect of details of
molecular structure on a transient detonation property. In addition, the
difference between the nongeminate propanes and the nongeminate butanes
gives a quantitative measure of the difference in failure diameter to be
expected between homologs. Although the particular compounds so far
investigated are not exact homologs, they do differ by CH_2 in molecular
formula.

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Suppose we raise a unit mass of each of two homologs to the same shock temperature T_s. This will not require the same shock pressure in the liquid, but the equations of state are very similar and the differences in pressure can be estimated from the densities of the liquids. Furthermore, since the active groups in the two compounds are identical, the kinetic factors Z and E_a are assumed to be the same. The specific heats of the two homologs can be assumed to be the same; C_v is about 0.35 cal/g for most organic materials at room temperature and we assume that a similar equality (at some other value) holds at shock temperature. Given all these assumptions, the main difference in the decomposition of homologs will then be in the heats of reaction. Finally, the heats of reaction can be assumed to be proportional to the number of difluoroamino groups present. The heats for the propanes and butanes would thus be roughly inversely proportional to the molecular weights:

$$Q_p = \frac{M_b}{M_p} \qquad Q_b \cong 1.1 \, Q_b$$

We are thus proposing that the reaction time t_r in Eq. (3) differs between homologs mainly because of a rather small difference in the effective heat of reaction, which, since it does not appear in the exponential, has little effect. The difference in failure diameter between the homologs also depends, under the theory, on the mechanical properties of the liquid and on the diameter effect to be assigned to it.

D. Dark Waves

In our last report we presented a photograph of a brass plate which had been in contact with a failing detonation in 1,2-DP. The ridges and depressions etched into the brass surface in the failure region corresponded to dark (failure) waves and regions of detonation respectively. The patterns are interpreted to show that:

1. The pressure in the dark waves is less than that in the detonation.
2. The pressure gradient across the boundary between dark regions and normal detonation is extremely sharp.

There are other features of these tests that are not yet properly understood. Perhaps the most serious reservation about their significance can be indicated by the observation that all of the dark waves in the small 1,2-DP charges apparently originate at the edges of the plate, corresponding to the right-angled corners of the wedge geometry of the test charge. The possibility remains that failure by dark waves applied in explosives as sensitive as 1,2-DP only in geometries involving discontinuities such as the corners of these wedge charges. (It has already been shown by streak photographs[4] that dark waves account for failures of IBA in smooth cylindrical charges.) We have made several attempts to construct a tapered cavity of circular cross section in a material which would permit recovery of the container after a test with 1,2-DP. The cavities produced so far have been so irregular that generation of dark waves can be practically assumed. It may well be that we will have to leave this last question concerning the presence of dark waves unresolved. Nevertheless we have investigated what the dark wave mechanism will mean to our theoretical treatment of failure diameter.

The main features of failure by dark waves have been worked out by Dremin.[5] Not all the postulates have been established with absolute certainty, but the general nature of this view seems reasonable. The connection with plane wave instability and with the somewhat clearer situation in gaseous detonations recommends application of this theory to the failure of difluoroamino liquids. Dremin first of all postulates that in a full-strength detonation wave there exists a mechanism to cause much faster reaction than would be produced by a smooth shock. Second, this mechanism is removed by some means whenever a dark wave appears. In the case we are trying to explain, the removal is related to the small diameter of the charge. In the dark wave, chemical reaction ceases. Third, failure of the charge will occur unless reinitiation takes place by the smooth shock mechanism. Finally, whether smooth shock initiation can take place depends on the diameter of the charge and the strength of the side rarefaction waves.

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The reignition of a detonation after the passage of a dark wave is illustrated in Fig. 14, which corresponds to a time-distance picture of detonation in a liquid column such as might be obtained with a streak camera in an end-on view. Consider what happens at the point F when the dark wave appears and, according to Dremin, chemical reaction ceases. Basing our opinion on the sharp etching on the brass plate referred to above, we suppose that the pressure drops suddenly at this point. Dremin postulates that a dark shock continues along the charge for a distance corresponding to the time between point F and point I. At point I re-initiation takes place in the smooth shock mode. According to the traces on the brass this is marked by a very sudden increase in pressure. Detonation spreads from point 1, eventually restoring the original wave over the entire area of charge.

Several difficulties arise in this interpretation which we have not satisfactorily resolved. The dark shock traveling beyond the point F cannot be moving at full detonation velocity. In fact, states in the dark region must lie somewhere on the unreacted Hugoniot for the liquid. We

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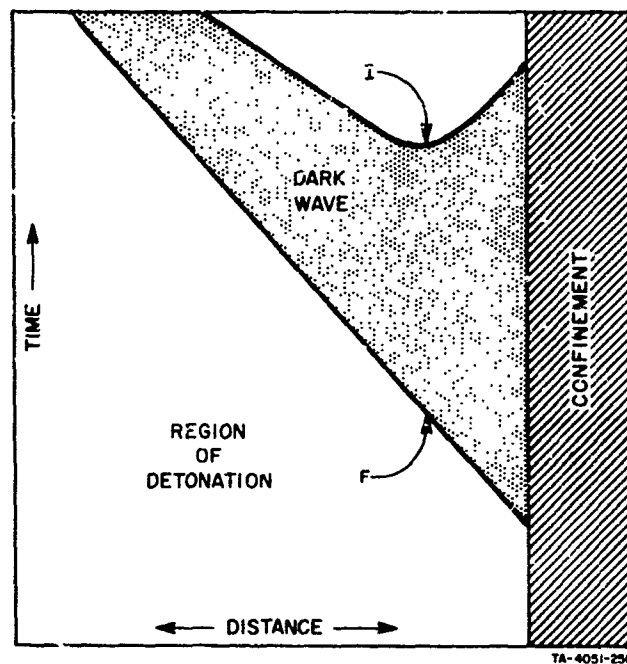
FIG. 14   DIAGRAM OF A DARK WAVE
IN A LIQUID EXPLOSIVE (U)

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have already noted evidence that the pressure is lower in the dark wave region; on the basis of this observation, the velocity of the dark wave should be considerably below that of the detonation wave. This seems to indicate that there is a feature of the process at points such as F which we are not detecting. In order to conserve momentum another wave is required at the transition point. Likewise, the sudden reinitiation of the wave at point I seems to call for introduction of momentum in the wave, and we have no direct experimental evidence as to how this is accomplished.

In spite of the fact that we do not yet understand the quantitative details in the appearance of dark waves and reinitiation of detonation, it is clear that we are dealing with the same general types of phenomena treated by the failure diameter theory discussed above. Quite obviously adiabatic explosion theory is involved in both cases. Although an adiabatic explosion of the normal type involving the usual induction time, is specifically denied in Dremin's theory of a full-strength wave, it comes into play within the dark wave. The question as to whether a runaway reaction can be achieved depends on how much lateral expansion takes place during the induction period. This in turn is determined by the diameter of the charge. Although we have not yet developed a way of estimating the shock strength within the dark wave, it is clear that the same mechanism we observe in our reaction-time measurements is operative there. It should be as easy to adapt reaction times to one case as to the other although the situations are obviously different.

E.   Reaction Times

In the paragraphs above it has been pointed out that reaction-time measurements made in shocked liquid explosives are pertinent to failure diameter theory, dark waves, and high temperature chemical kinetics in the liquid phase. During the past six months a number of reaction time tests have been run on nitromethane. Initial tests have been performed on IBA and 1,2-DP and this work is continuing. The information obtained has confirmed the earlier work performed with a different donor-attenuator system[6] and clarified several points in the experimental technique which needed resolution before the final data could be collected.

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Our first aim was to prove out reaction chambers that would eliminate wall-induced detonations without requiring the tedious construction necessary for the so-called "wall-less" containers discussed in earlier reports. Because of the availability of reasonable quantities of some of the difluoroamino compounds, we now propose to use squat, cylindrical test chambers of greater diameter than the donor. Experiments performed in 3-inch boxes and in $2\frac{1}{2}$- and $2\frac{1}{4}$-inch I.D. tubing are recorded in Table IV.

Table IV

COMPARISON OF REACTION TIMES IN THREE TYPES OF CONTAINERS

(Attenuator thickness 19.05 mm)

Container Size and Shape	Reaction Time (μsec)
3" cube	0.66
	0.38
	0.72
$2\frac{1}{2}$" cylinder	0.28
	0.31
$2\frac{1}{4}$" cylinder	0.28[*]
	0.38

[*]Corrected for temperature.

Reaction times for the three geometries are not significantly different. In contrast to the wall detonations that arose in previous tests with 1-inch I.D. tubing, no wall detonations were seen in these later tests. This is taken to indicate that the shocks traveling near the walls at the greater distances from the edge of the donor were sufficiently attenuated to avoid reaction.

During the container tests and in other preliminary experiments it became apparent that results with the new donor-attenuator system will not

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correspond exactly with those obtained with the old system. This is understandable since we are now generating a higher shock pressure in the donor and attenuating it with a larger run in plastic. The wave we introduce into the explosive has approximately the same peak pressure as before but in general has a flatter top. The calibration curves for the two systems are drawn in Fig. 15, and a comparison between the two systems is given by the selected data listed in Table V. The range of observable reaction times is restricted by the new wave form and it is possible to initiate detonation with lower peak pressures which are presumably compensated by a lower pressure gradient behind the shock front. The restricted range is consistent with data obtained on plane waves with quite flat tops. In the latter case the entire range of initiation phenomena from instant detonation to complete failure lay within a pressure range of less than 2 kbar.

It also became apparent during our technique studies that good temperature control would be necessary. The reaction cells are therefore being constructed in the manner illustrated in Fig. 16, with an annular chamber to hold a temperature-controlling medium. Salted ice is being used at present. Measurements at a higher controlled temperature will be undertaken soon.

F. Future Work

Full emphasis is now being placed on measurement of reaction times in shocked difluoroamino liquids. Shots at two temperatures are planned on IBA. Availability of 1,2-DB allows a comparison of this compound with 1,2-DP. Measurements will also be made on 2,2-DP and 2,2-DB. It will probably be possible to compare IBA with its next higher homolog, 1,2-MDB.

If sufficient material remains after the reaction-time measurements have been completed, failure diameters will be determined for 1,2-DB and 2,2-DB.
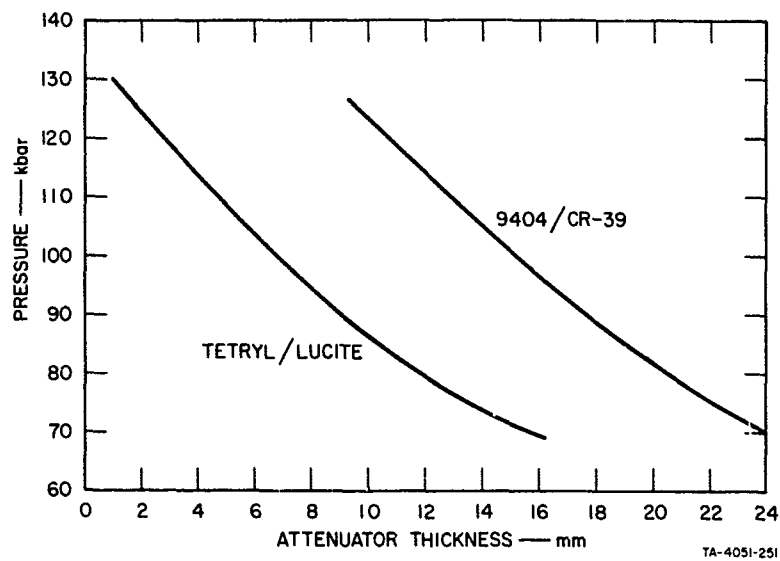
FIG. 15 CALIBRATION CURVES FOR TWO DONOR-
ATTENUATOR SYSTEMS (U)
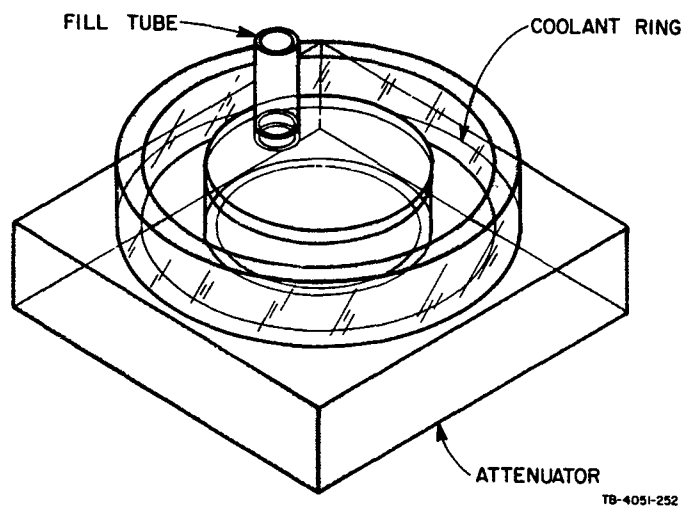
FIG. 16 CONTAINER FOR REACTION TIME MEASUREMENTS
WITH PROVISION FOR TEMPERATURE CONTROL (U)

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Table V

REACTION TIMES IN SHOCKED NITROMETHANE[*]

Attenuator Peak Pressure (kbar)	Reaction Times (μsec)	
	Tetryl Donor	PBX-9404 Donor
125	0	
117	0.34	
110	0.36 0.40	
103	1.08 1.19 1.49 1.66	
97	1.78 2.10 3.47	0
94		0.10 0.24
92	Fail	
86		0.38 0.66 0.72
82		0.39 1.33
80		Fail

[*]Experiments conducted in 3-inch cubical boxes.

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IV KINETICS OF DECOMPOSITION OF NF COMPOUNDS

(S.K. Brauman and M.E. Hill)

A. Introduction

The decomposition behavior of NF compounds under various conditions is of considerable interest, particularly as it relates to the handling, storage, and sensitivity of this class of compounds. One decomposition process which frequently occurs during long-term storage of these materials is dehydrofluorination. We have been studying the kinetics of this dehydrofluorination reaction in aqueous solution in order to relate the molecular structure of NF compounds to chemical reactivity (defined as ability to lose hydrogen fluoride) and possibly to sensitivity. The kinetic data indicate a distinct difference in chemical reactivity between vicinal and geminal compounds; this distinction also reflects the patterns found in the sensitivity studies in other phases of this project. Both homogeneous and heterogeneous dehydrofluorination of aliphatic NF compounds are relatively facile. The present studies also emphasize the significance of the container composition in catalyzing such decompositions.

We have just begun an investigation of the decomposition behavior of NF compounds under the influence of ultraviolet irradiation. As part of our studies on the basic properties and chemistry of NF_2 compounds, we are interested in the general behavior and reactivity of these propellant ingredients under such a stimulus. These studies might also provide useful information for the VLPP work. (Very little work has been reported to date on the photolysis of NF compounds.)

B. Discussion

1. Dehydrofluorination

The long-term storage stability of NF compounds is of considerable practical importance. The decomposition of NF compounds is generally quite surface-sensitive. It has been found that aluminum, stainless steel,

copper, Pyrex, and even Monel surfaces catalyze decomposition of these propellant ingredients in the gas phase, in solution, and in neat liquid. Once initiated, such decomposition is often autocatalytic. Under storage conditions, decomposition might be slow. In actual practice, however, storage over long periods of time could result in significant loss of active NF material. In addition, the relative sensitivity of the resultant decomposition products could alter the performance of the propellant.

Wall-catalyzed, heterogeneous decompositions of NF compounds often involve loss of hydrogen fluoride across the carbon-nitrogen bond at the NF_2 group. In some cases autocatalysis has been attributed to the hydrogen fluoride. Dehydrofluorination products with a remaining high NF_2 content, geminal bis-NF_2 grouping, and/or trifluoroamidine function are still quite sensitive.

We are studying the dehydrofluorination of NF compounds under controlled, homogeneous conditions. A knowledge of the kinetics and mechanism of this reaction under these conditions should provide some insight into the general problem of long-term storability of this class of compounds. Our experiments have been in aqueous solution, 70% water-30% diethylene glycol dimethyl ether (diglyme), over the temperature range 50°to 75°C. The dehydrofluorination is general base catalyzed. In the aqueous system employed in this work, the solvent water acts as the base and the kinetics are pseudo first-order. No autocatalysis has been observed in this work in aqueous solution. To date, eight bis- and tris-NF_2 propanes and butanes have been studied. The isomers possess vicinal (2,3-DB, 1,2-DP, 1,3-DP, IBA), geminal (1,1-DP, 2,2-DP), and effective mono-NF_2 (2,2,3-TB, 1,2,2-TP) functions. During the last half-year, the dehydrofluorination kinetics have been determined and the products have been identified for compounds 1,2,2-TP, 2,2,3-TB, and 1,3-DP. The details of this work are presented in the experimental part of this section. The kinetic data for total dehydrofluorination at 50°C for all the NF compounds studied are summarized in Table VI.

These rates for dehydrofluorination are unusually fast for elimination reactions in which water is acting as the base. This emphasizes the fact that moisture should be excluded from NF materials that can undergo

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Table VI

RELATIVE RATES FOR TOTAL DEHYDROFLUORINATION
IN 30% DIGLYME-70% WATER, 50°C

Code Name	Compound	Relative Rate of Dehydrofluorination
1,1-DP	C-C-C with X above and X below (on third C)	300
2,2,3-TB	C-C-C-C with X,X above (on 2nd,3rd C) and X below (on 3rd C)	15
2,3-DB-1	C-C-C-C with X X above (on 2nd,3rd C)	9
1,2,2-TP	C-C-C with X above (2nd C) and X X below (2nd,3rd C)	8
1,2-DP	C-C-C with X X below (2nd,3rd C)	4
1,3-DP	C-C-C with X below (1st and 3rd C)	3
IBA	C-C-C with C above (2nd C) and X X below (2nd,3rd C)	1 (1.8 x 10^{-5} sec^{-1})
2,2-DP	C-C-C with X above and X below (2nd C)	---

X = NF$_2$

dehydrofluorination. Reaction with stronger bases is even more rapid. Apparently it is the basic character of the free fluoride ion which makes the elimination autocatalytic under certain reaction conditions.

Certain generalizations can be drawn from the information in Tables VI and VII. Vicinal bis and tris isomers (these particular tris isomers, 1,2,2-TP and 2,3,3-TB, have only one reactive site for dehydrofluorination, effectively reducing them to very reactive mono compounds) fall in the same general range of reactivity. Internal, geminal compounds with no available active hydrogens (2,2-DP) are, of course, inert under these reaction conditions. On the other hand, terminal, geminal compounds (1,1-DP) are extremely reactive. This difference in chemical reactivity between vicinal and geminal NF compounds is more pronounced when data are corrected statistically for the total number of reactive hydrogens (Table VII). This observed distinction in chemical reactivity, defined as ability to lose hydrogen fluoride, parallels the difference in sensitivity of these two classes. Geminal compounds are generally much more sensitive than the vicinal NF_2 analogues.

The relative rates in Table VII also show that dehydrofluorination at a secondary site (2,2,3-TB) is some three and one-half times faster than that at a primary site (1,2,2-TP), per hydrogen at the reactive site. Both inductive and steric effects are important in determining the rate of elimination. Although additional NF_2 groups in a molecule enhance the rate of dehydrofluorination, branching adjacent to the reactive site tends to depress the rate. It is difficult to factor out these two effects from existing data. However, future work on the primary and secondary mono-difluoroaminobutanes, and 1,3,3-tris(difluoroamino)butane, (1,3,3-TB) and the trimethylethylene adduct (TMEA) should prove most illuminating in this matter.

The similarity of activation parameters (Table VIII) indicates that the transition states for dehydrofluorination are quite similar for all of the compounds studied. In general, loss of the first molecule of hydrogen fluoride is rate-determining. This elimination is concerted.[1] In the

Table VII

RELATIVE RATES FOR TOTAL DEHYDROFLUORINATION,
PER REACTIVE HYDROGEN AT THE REACTION SITE, 50°C

Code Name	Compound	Relative Rates			
1,1-DP	C-C-C with X above and X below terminal C	500			
2,2,3-TB	C-C-C-C (X above 2nd C; X, X below 2nd and 3rd C)	22	3.6	3.1	
2,3-DB-1	C-C-C-C (X, X below 2nd and 3rd C)	7.2		1	
1,2,2-TP	C-C-C (X above 2nd C; X, X below)	6.1	1		8.1
1,2-DP	C-C-C (X, X below)	(1.8)			
1,3-DP	C-C-C (X below 1st and 3rd C)	1			
IBA	C-C-C (C above center; X, X below)	0.76			1
2,2-DP	C-C-C (X above, X below center C)	------			

$X = NF_2$

Table VIII

ACTIVATION PARAMETERS FOR TOTAL DEHYDROFLUORINATION
IN 30% DIGLYME-70% WATER

Code Name	$\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta F^{\ddagger}$ (kcal mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
2,2,3-TB	15.4	24.3	-27.6
2,3-DB-1	15.1	24.6	-29.3
1,2,2-TP	14.9	24.7	-30.3
1,2-DP	16.7	25.2	-20.5
1,3-DP	15.5	25..	-30.5
IBA	14.8	26.0	-31.6

transition state, both carbon-hydrogen and nitrogen-fluorine bond-breaking occur and there is some carbon-nitrogen double bond character. Water acts as the base to remove the proton and the incipient fluorine ion is solvated (Fig. 17).

A surface with polar sites capable of coordinating with not only the hydrogen, but also the fluorine should be very effective at promoting dehydrofluorination. Of course, a surface with basic sites will also be most effective in catalyzing such a decomposition. Under the present reaction conditions, we have found Teflon vessels to be quite inert.
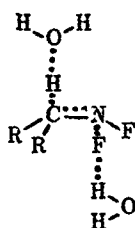
FIG. 17 TRANSITION STATE FOR DEHYDROFLUORINATION (C)

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2. Photolysis

Both N-chloro-[2] and N-bromoamines[3] exhibit weak absorptions in the
near ultraviolet. We have also found this to be true of N-fluoroamines.
In mixed hexanes, 2,3-DB-1 shows an absorption at 202-203 mμ (ϵ = 220);
t-BD in n-heptane absorbs at 215 mμ (ϵ = 40). Minnesota Mining and
Manufacturing Co. (3M) has examined the ultraviolet spectra of some NF
compounds, mostly perfluoro ones, which also show weak absorptions.[4]
3M reports that N-fluoroimines and certain difluoroamines are destroyed
by high frequency ultraviolet irradiation. The mechanism of this decompo-
sition is not known, however.

We have just initiated studies on the photolysis of NF compounds in
an attempt to determine the nature of this decomposition. Only preliminary
results for t-BD are now available. Both in n-heptane solution and in the
gas phase, t-BD is destroyed by irradiation from an unfiltered mercury
lamp. The gaseous decomposition appears to be considerably faster than
the solution decomposition. Except for differing amounts, the five pro-
ducts found in the gas phase photolysis are the same as those found in
solution. These include isobutane, isobutylene, and possibly hydrogen
cyanide. Not all of the products have been identified; consequently,
little can be said concerning the nature of the reaction. Considering
the high absorption frequency and low extinction coefficient of t-BD,
its decomposition is unusually efficient. A gas phase vacuum ultraviolet
spectrum of t-BD must be obtained; it could be that excitation involves
dissociation of the molecule.

C. Experimental Work

1. 1,3-DP

In the last report,[5] evidence was presented indicating that malononitrile
was the product of decomposition of 1,3-DP in aqueous solution. Kinetic data
and activation parameters have now been obtained for this dehydrofluorination
of 1,3-DP in 30% diglyme-70% water between 50° and 75°C. The reactions were
run using solutions that were approximately 8 x 10^{-3} $\underline{M}$ 1,3-DP. Aliquots
(15.0 ml) were withdrawn from the reaction mixture and extracted with methylene
chloride (2.0 ml). The organic extracts were then analyzed by glc. The

disappearance of 1,3-DP was followed using a 20% didecylphthalate column (42/60 chrom FB, 77°C). The malononitrile could only be detected by using a 20% phenyldiethanolamine succinate column (30/60 Chrom P, 193°C).

At 50°C, the disappearance of 1,3-DP followed first-order kinetics to over 90% reaction with a rate constant of 4.68×10^{-5} sec^{-1}. The solution remained colorless throughout the reaction. However, the yield of malononitrile was poor. Malononitrile is known to decompose under these conditions,[5] but the disappearance of 1,3-DP is some 30 times faster.

At 75°C, the linearity of the kinetics was equally as good. This rate constant for disappearance of 1,3-DP is 3.71×10^{-4} sec^{-1}, about 50 times larger than that for disappearance of malononitrile. The yield of this product was approximately 37%. In this case, the solution turned yellow, but only after very long reaction times.

The activation parameters calculated for the total disappearance of 1,3-DP are included in Table VIII. These values are quite similar to the others listed for various dehydrofluorination reactions. Consequently, the transition states for all these reactions are probably similar, describing the initial, rate-limiting loss of hydrogen fluoride (Fig. 17). Therefore, the first step in the decomposition of 1,3-DP is elimination of hydrogen fluoride, although the final yield of malononitrile is low (four molecules of hydrogen fluoride must be lost to produce malononitrile). The glc response characteristics and distribution coefficient of malononitrile between methylene chloride and 30% aqueous diglyme were determined in order to obtain a good estimate of this final yield of malononitrile . Not only does malononitrile decompose under these reaction conditions, but presumably some or all of the intermediates formed after the rate-limiting step also decompose.

2. 1,2,2-TP

Preliminary results on the dehydrofluorination of 1,2,2-TP were included in our last report.[5] Handling techniques were described for this sensitive material; 1,2,2-TP is only handled in dilute solution (diglyme or sym TCE). The preparation, isolation, and characterization of the dehydrofluorination product, DDP, were also described. The kinetics for the

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dehydrofluorination reaction have now been determined in 30% diglyme-70% water at 50° and 75°C. The low solubility of 1,2,2-TP in this reaction mixture necessitated the use of solutions which were only 4×10^{-3} $\underline{M}$ 1,2,2-TP. This was determined by varying the concentration of 1,2,2-TP, the concentration of diglyme, and the extraction solvent for the reaction. In the kinetic work, nitrobenzene was used as extraction solvent (2.0 ml solvent per 15.0 ml aliquot). The organic extracts were dried over anhydrous calcium chloride and were then analyzed by glc (20% GE-SF-96 on 60/80 firebrick, 53°C). The yield of the nitrile, DDP, was essentially quantitative in all cases. Although the glc response characteristics and distribution coefficient of DDP were measured, the actual yield of DDP could not be accurately determined since the starting material was always handled in solution and its glc characteristics and distribution coefficient were not known.

At 50°C, the rate of dehydrofluorination of 1,2,2-TP was linear for 80% reaction. The first-order rate constant is 1.44×10^{-4} sec^{-1}. The rate of disappearance of 1,2,2-TP was also equal to the rate of appearance of DDP ($k = 1.46 \times 10^{-4}$ sec^{-1}). At 75°C, the dehydrofluorination of 1,2,2-TP followed first-order kinetics to over 90% reaction ($k = 8.14 \times 10^{-4}$ sec^{-1}). At this temperature, the DDP decomposed slowly. In a 30% aqueous diglyme solution which was 3.8×10^{-3} $\underline{M}$ DDP and 7.3×10^{-3} $\underline{M}$ HF (two molar excess), the first-order rate constant for disappearance of DDP was 6×10^{-6} sec^{-1}, at 75°C.

The activation parameters for dehydrofluorination of 1,2,2-TP are given in Table VIII.

3.   2,2,3-TB

This compound was always handled in dilute solution; it was stored in methylene chloride. For kinetic purposes, a stock solution of 2,2,3-TB in diglyme was prepared. The methylene chloride solvent was carefully distilled off the 2,2,3-TB at atmospheric pressure. The last traces were removed at reduced pressure. The residue (99% pure 2,2,3-TB) was then diluted with diglyme. Aliquots of this diglyme stock solution were then appropriately diluted again with diglyme and water for each kinetic run.

The dehydrofluorination kinetics for 2,2,3-TB ($\sim 4 \times 10^{-3}$ $\underline{M}$) were determined in 30% diglyme-70% water at 50° and 75°C. Nitrobenzene was used as extraction solvent (2.0 ml solvent per 15.0 ml reaction aliquot). The organic extracts were analyzed using a 20% GE-SF-96 column on 60/80 firebrick at 60°C. Again the yields of the N-fluoroimine, FDB, could not be determined quantitatively, but they appeared to be quite high. Over this temperature range(50°-75°C), the FDB formed during the reaction slowly decomposed. Consequently, rates could not be obtained for appearance of product. At 50°C, the rate of disappearance of 2,2,3-TB exhibited first-order kinetics to more than 90% reaction with a rate constant of 2.58×10^{-4} sec^{-1}. At 75°C, this rate constant became 1.62×10^{-3} sec^{-1}. The activation parameters for this dehydrofluorination reaction are listed in Table VIII.

The dehydrofluorination product, FDB, was independently prepared and characterized. A 5 ml sample of the methylene chloride stock solution (13 g 2,2,3-TB in 90 g CH_2Cl_2) was diluted with an additional 20 ml methylene chloride. Pyridine (4 ml) was added and the resulting solution was heated under reflux for about one hour. The reaction was quenched by pouring the mixture onto ice. After repeated extraction with 5% hydrochloric acid and then with water, the reaction mixture was dried over sodium sulfate and calcium chloride. The excess solvent was distilled off and the FDB was isolated and purified by gas phase chromotography (20% GE-DF-96 on 60/80 firebrick, 53°C). Only one product peak was observed by glc. The elemental analysis of this FDB could not be obtained because the sample always detonated on heating. However, the infrared spectrum of neat FDB showed carbon-nitrogen double bond absorption at 1630 cm^{-1}. The proton nmr also analyzed for the expected N-fluoroimine. There was a doublet (J = 6.0 cps) at 7.83 τ for $-\underset{\underset{NF}{\|}}{C}-CH_3$ and a quintet (J = 2.0 cps) at 8.12 τ for $-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-CH_3$. The FDB apparently contained only one geometric isomer-- presumably the more sterically favorable $\underline{syn}$ isomer.

4. Photolysis of t-BD

The photolytic studies have just begun. An unfiltered, immersion, quartz mercury lamp (pen-ray lamp, Ultraviolet Products, Model 11-SC-1, ~ 10 watt)was used for all the work discussed here. The irradiations were run at 0°C, in an ice-water bath.

a. **Solution.** One photolytic reaction was run on a n-heptane solution of t-BD (4.6×10^{-2} M). Over a total irradiation time of 11 hours, aliquots were withdrawn from the reaction mixture and analyzed by glc (20% didecyl-phthalate column, 56°C). After approximately four hours of irradiation, the t-BD was 10% decomposed. Six decomposition products were detected, three being major peaks on the glc. Two products were identified by peak enhancement upon addition of known material to the samples. One major product was isobutylene; a minor one was isobutane. Another major product might be hydrogen cyanide.

b. **Gas Phase.** Two photolyses were run on degassed, gaseous samples of t-BD (approximately 50 mm Hg at 0°C). One reaction was stopped after 30 minutes, the other after four hours. The reaction mixtures were then dissolved in n-heptane and analyzed by glc. After four hours of irradiation, the t-BD was completely destroyed. There was a brown coating on the light probe and the material balance for the reaction appeared poor. The five products observed were among those found in the solution photolysis. Isobutylene, isobutane, and possibly hydrogen cyanide were minor products in the gas phase reaction.

The same five product peaks were also observed by gas chromatography after only 30 minutes of irradiation. The t-BD was still the major peak. Of the five products, three were major peaks, including isobutane and isobutylene. Again, there was some deposit on the light probe.

Except for differing amounts, the products found in the gas phase photolyses of t-BD are the same as those found in solution. All the products still have to be identified and conditions must be found where only homo-geneous reactions occur. Local heating by the light source may be a problem and a different type of lamp (water-cooled or external source) may have to be used.

D. Future Work

The kinetics studies on the dehydrofluorination of NF compounds will continue as compounds (1-MB, 1,3,3-TB, TMEA) become available. The trimethylethylene adduct will be examined next. The photolytic studies on t-BD will also continue. Optimal reaction conditions must be obtained and products must then be identified. It might be of interest to run the photolysis in the presence of certain additives (N_2F_4, F_2); perhaps a chain reaction could be initiated.

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4. (a) 3M, QR-8, January-March 1961, Nord 18688; (b) 3M, QR-9, April-June, 1961, Nord 18688; (c) 3M, QR-10, July-September, 1961, Nord 18688.
5. Stanford Research Institute, Project 4051, Technical Progress Report 66-4 (Quarterly), "Sensitivity Fundamentals (U)," June 15-September 14, 1966 (C).

V VERY LOW PRESSURE PYROLYSIS (VLPP)

(D.S. Ross, T. Mill, M.E. Hill)

A. Introduction

In our last report[1] we discussed the very low pressure pyrolysis (VLPP) of 2,2-DP, $\underline{t}$-butyldifluoramine, and 1,1-DP. We reported that, at 560°C, 2,2-DP initially undergoes C-N scission, yielding $(CH_3)_2(NF_2)C\cdot$ which rearranges subsequently to yield $(CH_3)_2(F)CNF$. Fragmentation of this species yields $\cdot CH_3$ and $CH_3\underset{\overset{\|}{NF}}{CF}$. A minor reaction path for $(CH_3)_2(NF_2)C\cdot$ was thought to be loss of fluorine to yield $(CH_3)_2C=NF$. The same initial C-N scission was suggested as the initial step in the decomposition of $\underline{t}$-butyldifluoramine, the radical fragments, $(CH_3)_3C\cdot$ and $\cdot NF_2$, then going to the products $(CH_3)_2C=CH_2$ and N_2F_4, respectively. Initial results with 1,1-DP suggested that it too initially lost an NF_2 group and that this was followed by fluorine migration and fragmentation.

B. Very Low Pressure Pyrolysis (VLPP) of $\underline{t}$-Butyldifluoramine

It was desirable to know the C-N bond strength for a material in which there was only one NF_2 group. Such information would enable us to determine the effect of further substitution of NF_2 on the C-N bond by comparing the results obtained with a mono-NF_2 material to those of the bis compounds already studied. In the following section these results are tabulated and discussed. The compound chosen for study was $\underline{t}$-butyldifluoramine. The VLPP of the material was studied from 600°-900°C in a quartz reaction vessel the geometry of which allowed an average of 110 collisions. The products isolated from the pyrolysis are $(CH_3)_2C=CH_2$ and N_2F_4. A minor product is $(CH_3)_3CH$.

Isolation of isobutylene and N_2F_4 from the decomposition of $\underline{t}$-butyldifluoroamine does not permit a clear distinction between an initial homolytic scission of the C-N bond to give radical fragments (A) and a four-center molecular elimination of HNF_2 (B).

(A) $\underline{t}$-BuNF$_2$ $\longrightarrow$ $\underline{t}$-Bu$\cdot$ + $\cdot$NF$_2$

$\underline{t}$-Bu$\cdot$ $\longrightarrow$ $(CH_3)_2C{=}CH_2$ + H$\cdot$

$2\dot{N}F_2$ $\longrightarrow$ N_2F_4

(B) $(CH_3)_2 - \overset{\overset{\displaystyle H_2C\ -\ H}{|}}{C} - NF_2 \longrightarrow \left[(CH_3)_2\ -\ \overset{\overset{\displaystyle H_2C\cdots\cdot H}{|\vdots\ \ \vdots}}{C}\cdots\cdot NF_2 \right] \longrightarrow (CH_3)_2C{=}CH_2 + HNF_2$

HNF_2 $\longrightarrow$ N_2F_4 + H_2
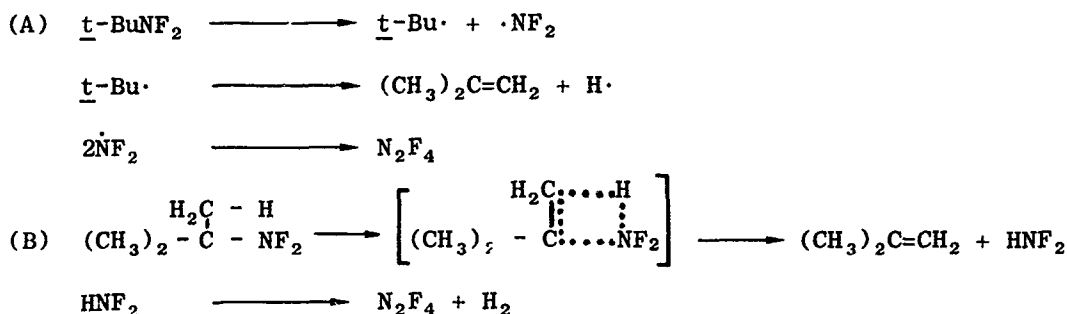
A kinetic distinction between (A) and (B) is possible. The Arrhenius A-factor for (B) should be one to four orders of magnitude smaller than that for (A) because of the cyclic transition state required for (B) with its concomitant loss of rotational entropy.

Since the reactor operates at a pressure of about 1 micron (somewhat below the high pressure limit for molecules of this size), simple analysis of the data does not yield useful high pressure kinetic parameters. However, the method of Benson and Spokes[2] provides a means of treating the data so as to yield an expression containing the high pressure values of A and E_a. If k_{uni} is the rate of unimolecular decomposition in our reactor,

$$k_{uni} = k_{ea} \frac{f}{1-f} \tag{1}$$

where k_{ea} is the rate of escape from the reactor and f is the fraction of unimolecular decomposition. The escape rate, k_{ea}, can be calculated from the known dimensions of the reactor and from kinetic theory. Substitution of k_{uni} into Eq. (2) then yields Q, which is substituted into Eq. (3).

$$k_{uni} = \frac{k_w}{2\sqrt{2\pi}} \left[\frac{eQ}{(n-1)RT} \right]^{n-1} \exp{-\left(\frac{Q}{RT} \right)} \tag{2}$$

$$\log A = \log k_w - (n-1) \log \left(1 - \frac{E_a}{Q} \right) \tag{3}$$

The rate of wall collisions, k_w, in our system is about $10^{4.5}$ sec^{-1}. The number of effective oscillators, n, is about 2/3 of the maximum

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number of internal vibrations in a molecule, or 2/3 (3N - 6) where N is the total number of atoms in the molecule.

In experiments with t-butyldifluoramine, at 780°C (1053°K) there is 41.7% decomposition. Substitution of this value into (1) and, with n = 28, subsequent use of Eqs. (2) and (3), yields

$$\log A = 4.5 - 27 \log \left[1 - \frac{E_a}{93.38} \right] \qquad (4)$$

Figure 18 is a graphical display of this expression, which represents a unique family af Arrhenius parameters for the unimolecular decomposition of t-butyldifluoramine. At this point it is necessary to consider mechanistic paths (A) and (B).
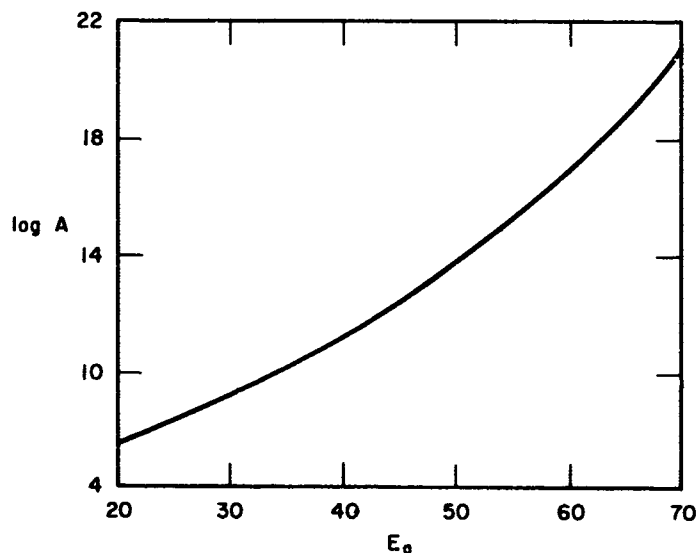

FIG. 18 PLOT OF LOG A vs. E_a FOR THE VLPP OF t-BUTYLDIFLUORAMINE (C)

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It is possible to estimate fairly well a value for the Arrhenius A-factor for reaction (B) by examining data for analogous reactions such as the pyrolyses of t-butyl halides (Table IX) which are known to proceed via molecular elimination of HX. The transition states for both HX and HNF$_2$ elimination are similar in that they involve a four-membered ring. Thus there are similar internal rotational degrees of freedom lost in
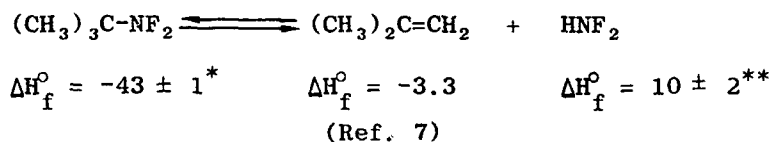
Table IX

UNIMOLECULAR GAS-PHASE DECOMPOSITIONS THAT
GIVE STABLE MOLECULES

$$(CH_3)_3C-X \longrightarrow (CH_3)_2C=CH_2 + HX$$

X	E_a (kcal/mole)	Log A (sec^{-1})	Reference
Cl	41.4	12.4	3
Br	40.5	13.3	4
	42.2	14.0	5
I	36.4	12.52	6

the transition states in both processes. Closer inspection shows that there is an even greater loss of rotational freedom in (B) than for the processes in Table IX, because of the rotational restrictions on -NF$_2$. No such restrictions are possible for the t-butyl halide cases. Thus (B) should have an even lower A-factor than those for the halides. If we consider a value of $10^{12.0}$ sec^{-1}, Eq. (4) gives $E_a = \sim44$ kcal/mole.

From the thermochemistry of B,

$$(CH_3)_3C-NF_2 \rightleftharpoons (CH_3)_2C=CH_2 + HNF_2$$

$$\Delta H_f^o = -43 \pm 1^* \qquad \Delta H_f^o = -3.3 \qquad \Delta H_f^o = 10 \pm 2^{**}$$
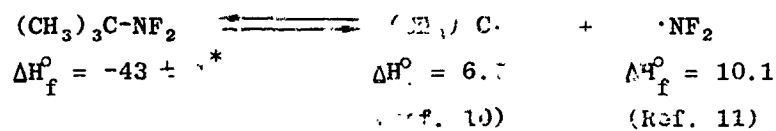$$(Ref. 7)$$

_____

*Estimated by method of group additivities.[8]
**Estimated from Trotman-Dickenson's value of 72.5 kcal/mole for D(H-NF$_2$)[9]
and thermochemical data for H and NF$_2$. (Refs. 10, 11)

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Inspection of the heat values shows the reaction is endothermic by about 30 kcal/mole. If the elimination process proceeds with an activation energy of ~44 kcal/mole, the reverse reaction, addition of HNF_2 across the double bond, must of course proceed through the same transition state, and must necessarily have an activation energy of ~14 kcal/mole. This value suggests that the addition should proceed easily at room temperature. In fact, the gas phase addition of HNF_2 across a double bond is unreported.[12] In view of the low activation energy it seems strange that there are no reported attempts to use this HNF_2 additive reaction. Therefore this suggests that the reaction is difficult, proceeding with an activation energy considerably greater than 14 kcal/mole. We therefore conclude that the four-center elimination is unlikely.

For the radical process, rou (A), a similar thermochemical analysis may be made:

$$(CH_3)_3C-NF_2 \rightleftharpoons (CH_3)_3C\cdot + \cdot NF_2$$

$$\Delta H_f^o = -43 \pm \cdot{}^* \qquad \Delta H^o = 6. \qquad \Delta H_f^o = 10.1$$

$$(Ref. 10) \qquad (Ref. 11)$$

The ΔH_f^o values indicate the reaction is endothermic by about 60 kcal/mole. Since radical combination reactions, such as the reverse of (A), occur with little or no activation energy,[13] the endothermicity must be close to the activation energy and equal to 60 kcal/mole. Substitution of this value of E_a in Eq. (4) gives an A factor of $10^{16.6}$ sec^{-1}. An A-factor of this magnitude is consistent with other unimolecular reaction which produce radicals.[14] These results are also consistent with the results of Rocketdyne workers who studied compounds H, R, T^{15} and $1,2-DP^{16}$ in a monel stirred-flow reactor.

We may conclude, therefore, that the unimolecular decomposition of t-butyldifluoramine, and probably of other alkyl difluoramines, proceeds by initial homolysis of a C-N bond. From thermochemical and VLPP kinetic data we obtain values for the high pressure Arrhenius parameters of:

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*Estimated by the method of group additivities.[3]

$$k = 10^{16.6 \pm 0.2} \left(\exp - \frac{(60 \pm 1) \times 10^3}{RT} \right) \qquad (5)$$

It is important to keep in mind that these parameters are only as precise as the thermochemical data used to generate them.

As additional evidence we note that in our reactor t-butyl radical, as generated by the pyrolysis of azoisobutane, decomposes primarily in a unimolecular manner, yielding isobutylene (plus, of course, a hydrogen atom). However, small amounts of isobutane are also formed, presumably in a bimolecular reaction. The small quantity of isobutane formed in the decomposition of t-butyldifluoramine thus suggests the presence of t-butyl radical, and therefore lends further support to our choice of mechanism.

C. Discussion of VLPP Results

The decomposition of the NF materials by VLPP occurs below the high pressure limit for molecules of this size. While activation energies may be obtained by making reasonable estimates of Arrhenius A-factors, it is probably more convenient to talk of the decomposition of these molecules in terms of the temperature at which the materials are 50% decomposed in our quartz hundred-collision reactor ($T_{\frac{1}{2}}$). Direct comparisons will be made in these terms in the following section of this report.

A summary of all the kinetic data obtained for NF compounds with the VLPP reactor is presented in Table X. The compounds are arranged in order of increasing $T_{\frac{1}{2}}$, i.e., in order of increasing stability of the C-N bond. If the materials are rearranged as in Table XI, some useful relationships emerge. The compounds are arranged in three columns in terms of similar structural features; the C-N bond under consideration is the heavy bond. In column A, if it is assumed that the effects of a methyl group and an ethyl group are about the same, we see that methyl is destabilizing with respect to hydrogen by about 3 kcal/mole. This result is reasonable in that the effect of substitution is stabilization of the transition state leading to a radical, and thus one would expect methyl to facilitate C-N homolysis with respect to hydrogen in these compounds.

Table X

STABILITY DATA

Compound	$T_{\frac{1}{2}}(^{\circ}C)$ [a]	LVD Gap Sensitivity[b] (cm)
2,2-DP	575[c]	> 187
IBA	650[c]	---
1,1-DP	~650	---
1,2-DP	740[c]	95
t-BuNF$_2$	845	---

[a]Temperature at 50% decomposition in our reactor.

[b]Steel confinement, $\frac{1}{4}$" wall.

[c]Data obtained by Benson and Spokes.[17]

Table XI

GROUP SUBSTITUTION EFFECT ON STABILITY[a]

A		B		C	
Compound	$T_{\frac{1}{2}}\ (^{\circ}C)$	Compound	$T_{\frac{1}{2}}\ (^{\circ}C)$	Compound	$T_{\frac{1}{2}}\ (^{\circ}C)$
2,2-DP $F_2N-C(CH_3)(CH_3)-NF_2$	575	2,2-DP $F_2N-C(CH_3)(CH_3)-NF_2$	575	1,1-DP $F_2N-C(H)(CH_2CH_3)-NF_2$	~650
1,1-DP $F_2N-C(H)(CH_2CH_3)-NF_2$	~650	IBA $CH_3-C(CH_3)(CH_2NF_2)-NF_2$	650	1,2-DP $CH_3-C(H)(CH_2NF_2)-NF_2$	740
		t-BuNF$_2$ $CH_3-C(CH_3)(CH_3)-NF_2$	815	sec-alkyl NF$_2$ $CH_3-C(H)(CH_3)-NF_2$	---

a. If an A-factor of $10^{16.6}$ is assigned, a difference of $100^{\circ}C$ corresponds roughly to about 5 kcal/mole in bond strength. The C-N bonds considered here are on the order of 50 kcal/mole.

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In column B of Table XI, the NF_2-bearing carbon is tertiary. The closer the second NF_2 group is to the first, the weaker is the C-N bond, with a $300°$ or 15 kcal total difference between 2,2-DP and $\underline{t}$-BuNF$_2$. Similarly, in column C, the closer the NF_2 groups, the less the stability. Although we have not investigated the decomposition of a sec-alkyl difluoroamine, we expect soon to obtain a sample of 2-difluoroaminobutane and study its pyrolysis.

These empirical rules governing structure and reactivity should prove generally useful for any series of difluoroamino alkanes. For example, in the general compound (C) the C-NF bond is weakened with respect to X = H when X = NF_2 or CH_3, and is stabilized by $n > 1$. A compound soon to be studied is 1,3-DP. According to these rules it should be the most stable

$$X_2C - NF_2$$
$$(CH_2)_n$$
$$CH_2NF_2$$
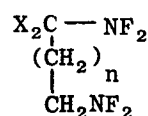
(C)

of the bis-difluoroamino compounds studied to date, for in it are embodied all of the stabilizing features we have discussed.

In the last column in Table X are listed LVD gap sensitivity data. These data are presented here in an attempt to correlate gap sensitivity with C-N bond strength. Although there are only two pieces of sensitivity data, they do fall in the proper order--material with the weaker C-N bond being the more sensitive. Additional gap sensitivity measurements on compounds listed in Table X ought to either confirm or deny our correlation.

D. Discussion of the Chemistry of the Detonation Process

Little is understood of the chemistry involved in a detonation. In the above section we have suggested that there is a correlation between the LVD gap sensitivity of a material and the strengths of the C-N bonds within the material. In a complete discussion of sensitivity, however, it is necessary to consider from a chemical point of view not only the initial endothermic step but the succeeding exothermic reactions which

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supply energy for the propagation of the reaction sequence. Such a consideration should explain such facts as why 2,2-DP is more sensitive than 1,2-DP, vide supra, while its failure diameter is greater than that of 1,2-DP (Ref. 18). Further, in regard to failure diameter, it is necessary to explain why the propane isomers fall into two classes--the geminates (2,2-DP; 1,2-DP) exhibiting the same failure diameter, and the nongeminates (1,2-DP; 1,3-DP) exhibiting a failure diameter different from the geminates, but the same as each other.[18]

We wish now to suggest a chemical model which may explain the failure diameter differences. The model is presented in Table XII.

Table XII

SUGGESTED MODEL FOR DETONATION CHEMISTRY

Nongeminate Compounds	Geminate Compounds
$RCH_2NF_2 \rightarrow R\dot{C}H_2 + \cdot NF_2$ (1)	$RCH_2C(NF_2)_2R' \rightarrow RCH_2\dot{C}(NF_2)R' + \dot{N}F_2$ (5)
$\cdot NF_2 \rightarrow \cdot F + \cdot \dot{N}F$ (2)	$\dot{N}F_2 \rightarrow \cdot F + \cdot \dot{N}F$ (6)
$\cdot F + RCH_2NF_2 \rightarrow HF + R\dot{C}HNF_2$ (3)	$\cdot F + RCH_2C(NF_2)_2R' \rightarrow HF + R\dot{C}HC(NF_2)_2R'$ (7)
$RCHNF_2 \rightarrow RCH=NF + \cdot F$ (4)	$R\dot{C}HC(NF_2)_2R' \rightarrow RCH=C(NF_2)R' + \dot{N}F_2$ (8)

Note the differences in the two mechanisms. For the nongeminate compounds a chain reaction is proposed which involves only ·F as the chain carrier and involves only steps (3) and (4). In the geminal case, there are two chain carriers, ·NF$_2$ and ·F, and three steps are required for the chain, steps (6), (7), and (8). While steps (7) and (8) roughly parallel steps (3) and (4) in exothermicity, step (6) is an endothermic step. Thus the chain process for the geminate materials includes an endothermic step, while that for nongeminates does not. The proposed chain process for the geminate should thus have a higher activation energy, i.e., be more sensitive to loss of energy. The failure diameter

data[18] correlate with this approach in that the geminates fail at ~4 mm while the nongeminates do not fail until a confinement of just under 2 mm is reached.

E.   Future Work

With this preliminary support of our model, we plan to undertake some studies in radical-initiated reactions of NF materials. It may be possible to initiate chain decomposition in these materials by generating alkoxy radicals within a sample. There is further the possibility of photo-chemical initiation.

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)*	2a REPORT SECURITY CLASSIFICATION
Stanford Research Institute	Confidential
	2b GROUP
	4

3 REPORT TITLE

Sensitivity Fundamentals (U)

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Semiannual, September 16, 1966 to March 15, 1967

5 AUTHOR(S) *(Last name, first name, initial)*

Amster, Adolph B.	Seely, Leslie B.	Ross, David S.	Berke, Joseph G.
Hill, Marion E.	Mill, Theodore	Woolfolk, Robert W.	
Evans, Marjorie W.	Brauman, Sharon K.	Tegg, Derek	

6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO OF REFS
April 15, 1967	86	39

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
Nonr 3760(00)	67-1
b PROJECT NO.	
SRI 4051	
c	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d	

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	Office of Naval Research Washington, D.C.

13 ABSTRACT

Low Velocity Detonations

The conventional gap test was used to investigate the importance of confinement material and geometry on the low velocity detonation (LVD) shock sensitivity of the difluoroamino compounds. Unusual results for 1,2-DP, summarized in this report, led to high speed framing camera studies of its LVD initiation. The photographs show that several initiation mechanisms influence the conventional gap test. These mechanisms are discussed in terms of confinement geometry and material as well as initial shock input. (U)

A relationship between the LVD gap sensitivity and initial decomposition kinetics is also discussed. (U)

Chemistry and Physics of Detonation

Concepts of transient detonation phenomena in the simple difluoroamino liquids underwent a change during the past six months. Adiabatic explosion theory is still basic for failure on liquids, but the concept apparently must be applied in a new way. Failure diameter studies on IBA and 2,3-DB have been completed, and the importance of dark waves in 1,2-DP has been partially elucidated. Reaction-time measurements on nitromethane have proved out suitable reaction chambers, demonstrated the effect of pressure profile on initiation behavior and indicated the necessity for careful temperature control. Final reaction-time measurements on 1,2-DP and IBA are in progress. (C)
(concluded on separate page)

DD _{FORM} **1473**
1 JAN 64

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT

Sensitivity
 NF Compound Sensitivity
 1,2-Bis(difluoroamino)propane
 2,3-Bis(difluoroamino)butane
 	
 NF Compounds
   Low Velocity Detonation
   Critical Failure Diameter
   Detonation Reaction Times
   Solution Decomposition Kinetics
   HF Elimination
   Very Low Pressure Pyrolysis
   Gap Sensitivity						

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ABSTRACT   (concluded)

Kinetics of Decomposition of NF Compounds in Aqueous Solution

In the kinetic studies of dehydrofluorination of NF compounds in aqueous solution, rates and activation parameters have now been determined for 1,3-DP, 1,2,2-TP, and 2,2,3-TB in 30% diglyme-70% water between $50°$ and $75°$C. To date, eight bis and tris propanes and butanes have been examined. Studies have also been initiated on the photolysis of NF compounds. Preliminary results for t-BD are available. (C)

Very Low Pressure Pyrolysis (VLPP)

A detailed kinetic study of the decomposition of t-butyl difluoramine via VLPP has been carried out. The decomposition yields, as major products, N_2F_4 and $(CH_3)_2C=CH_2$; a minor product is $(CH_3)_3CH$. We conclude from the study that the pyrolysis proceeds through homolysis of the C-N bond and follows the rate law

$$k = 10^{16.6 \pm 0.2} \left(\exp - \frac{(60 \pm 1) \times 10^3}{RT} \right)$$

Inspection of the summary of VLPP data for the compounds 2,2-DP, IBA, 1,1-DP, 1,2-DP, and t-BuNF$_2$ allows us to conclude that the C-N bond in an alkyl difluoroamino compound is weakened both by replacement of hydrogen by carbon on the NF$_2$-bearing carbon and by a close proximity of NF$_2$ groups within the same molecule. (C)

A chemical model involving chain processes for detonation propagation is proposed to explain failure diameter differences between geminal and nongeminal NF compounds. It is suggested that detonation propagation in the nongeminal compounds proceeds by means of a chain with fluorine atoms as chain carrier, and that detonation in the geminal compounds proceeds via a chain with both F and NF$_2$ as chain carriers. (C)